

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

CALLAWAY GOLF COMPANY,

Plaintiff,

v.

ACUSHNET COMPANY,

Defendant.

C. A. No. 06-91 (SLR)

REDACTED

**DECLARATION OF THOMAS L. HALKOWSKI IN SUPPORT OF
CALLAWAY GOLF'S MOTION *IN LIMINE* TO PRECLUDE ANY REFERENCE TO
ACUSHNET'S "TEST BALLS"**

I, Thomas L. Halkowski, declare as follows:

1. I am a member of Fish & Richardson P.C., counsel of record in this action for Callaway Golf Company ("Callaway"). I am a member of the Bar of the State of Delaware and am admitted to this Court. I have personal knowledge of the matters stated in this declaration and would testify truthfully to them if called upon to do so.

2. **Attached as Exhibit 1** is a true and correct copy of United States Patent 5,885,172, to Hebert et al., dated March 23, 1999, bearing production numbers CW00300663-CW00300669.

3. **Attached as Exhibit 2** is a true and correct copy of United States Patent 5,820,489, to Sullivan et al, dated October 13, 1998.

4. **Attached as Exhibit 3** is a true and correct copy of United States Patent 5,932,038, to Bach et al., dated August 3, 1999.

5. **Attached as Exhibit 4** is a true and correct copy of United States Patent Publication Number US 2004/0048688 A1, to Hogge et al, dated March 11, 2004.

6. **Attached as Exhibit 5** is a true and correct copy of the Non-Confidential Brief of Defendant-Appellant Acushnet Company in Federal Circuit Appeal No. 2009-1976, dated January 26, 2009.

7. **Attached as Exhibit 6** is a true and correct copy of excerpts from the deposition transcript of Jeffrey L. Dalton, dated October 16, 2007.

I declare under penalty of perjury that the foregoing is true and correct.

Executed this 11th day of December, 2009 at Wilmington, Delaware.

Dated: December 11, 2009 FISH & RICHARDSON P.C.

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CERTIFICATE OF SERVICE

I hereby certify that on December 11, 2009, the attached document was electronically filed with the Clerk of Court using CM/ECF which will send electronic notification to the registered attorney(s) of record that the document has been filed and is available for viewing and downloading.

I hereby certify that on December 11, 2009, the attached document was electronically mailed to the following person(s):

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**DECLARATION OF THOMAS L. HALKOWSKI
IN SUPPORT OF CALLAWAY GOLF'S
MOTION *IN LIMINE* TO EXCLUDE
ACUSHNET'S "TEST BALLS" AND RELATED
TESTIMONY**

EXHIBIT 1



US005885172A

United States Patent [19]

Hebert et al.

[11] **Patent Number:** 5,885,172[45] **Date of Patent:** Mar. 23, 1999[54] **MULTILAYER GOLF BALL WITH A THIN THERMOSET OUTER LAYER**[75] Inventors: **Edmund A. Hebert**, North Dartmouth, Mass.; **William E Morgan**, Barrington, R.I.; **Dean Snell**, Oceanside, Calif.[73] Assignee: **Acushnet Company**, Fairhaven, Mass.[21] Appl. No.: **863,788**[22] Filed: **May 27, 1997**[51] Int. Cl.⁶ **A63B 37/08**; A63B 37/12; A63B 37/06[52] U.S. Cl. **473/354**; 473/365; 473/363; 473/376; 473/378[58] Field of Search **473/377, 378, 473/384, 354, 363, 365, 374, 376**[56] **References Cited****U.S. PATENT DOCUMENTS**

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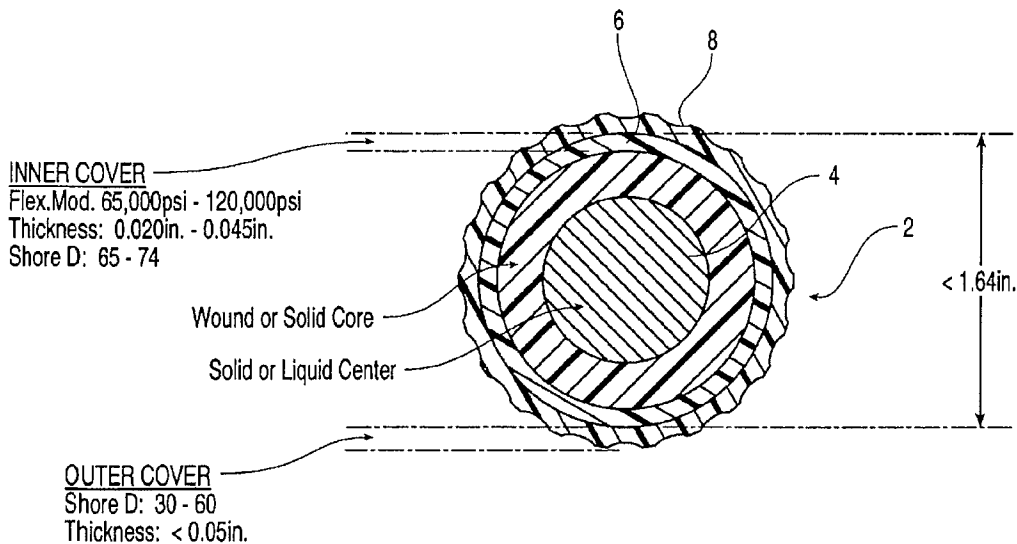
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Primary Examiner—George J. Marlo*Attorney, Agent, or Firm*—Pennie & Edmonds LLP[57] **ABSTRACT**

The present invention is directed towards a multilayer golf ball which comprises a core, an inner cover layer and an outer cover layer, wherein the outer cover layer comprises a thermoset material formed from a castable, reactive liquid, said outer layer having a thickness of less than 0.05 inches and said inner cover layer comprises a high flexural modulus material. The golf balls of the present invention are believed to provide a "progressive performance" from driver to wedge.

18 Claims, 1 Drawing Sheet

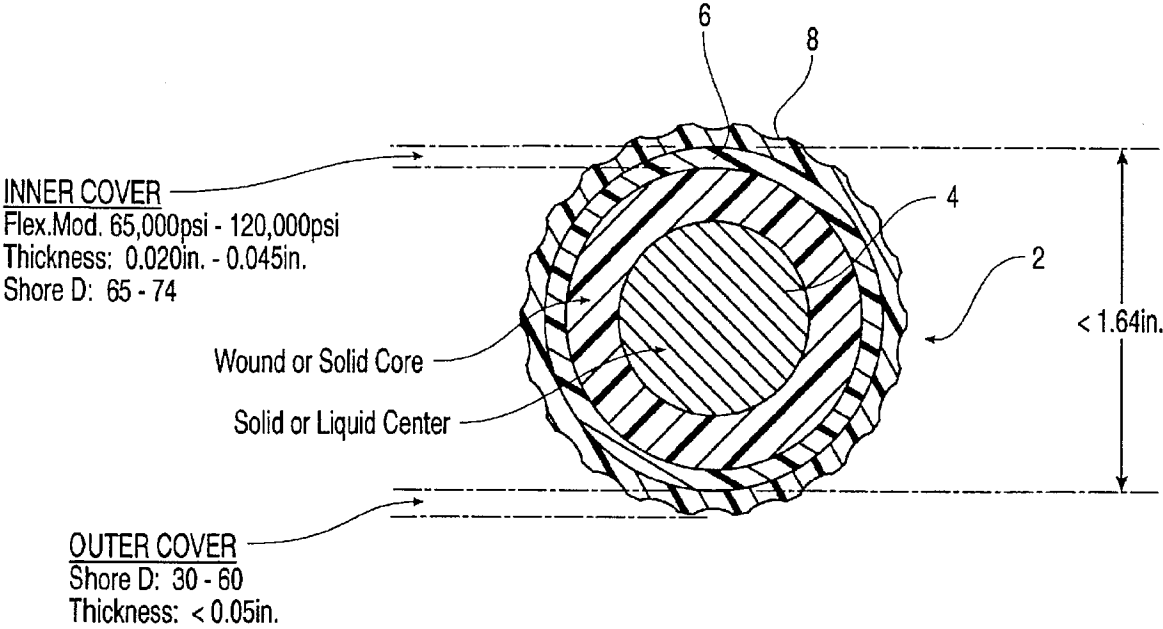


FIG. 1

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MULTILAYER GOLF BALL WITH A THIN THERMOSET OUTER LAYER

FIELD OF INVENTION

This invention relates generally to golf balls, and more specifically, to a multilayer golf ball. In particular, this invention relates to a golf ball having a core, an inner cover layer and a very thin outer cover layer, wherein the outer cover layer comprises a thermoset material formed from a castable, reactive liquid and the inner cover layer comprises a high flexural modulus material. The multilayer golf balls of the present invention provide "progressive performance" characteristics when struck with golf clubs of varying head speed and loft angle.

BACKGROUND OF THE INVENTION

Until recently golf balls were typically divided into two general types or groups: 1) two piece balls and 2) wound balls (also known as three piece balls). The difference in play characteristics resulting from these different types of constructions can be quite significant.

Balls having a two piece construction are generally most popular with the recreational golfer because they provide a very durable ball while also providing maximum distance. Two piece balls are made with a single solid core, usually formed of a crosslinked rubber, which is encased by a cover material. Typically the solid core is made of polybutadiene which is chemically crosslinked with zinc diacrylate and/or similar crosslinking agents. The cover comprises tough, cut-proof blends of one or more materials known as ionomers such as SURLYNs®, which are resins sold commercially by DuPont or Iotek® which is sold commercially by Exxon.

The combination of the above-described core and cover materials provides a "hard" covered ball that is resistant to cutting and other damage caused by striking the ball with a golf club. Further, such a combination imparts a high initial velocity to the ball which results in increased distance. Due to their hardness however, these balls have a relatively low spin rate which makes them difficult to control, particularly on shorter approach shots. As such, these types of balls are generally considered to be "distance" balls. Because these materials are very rigid, many two piece balls have a hard "feel" when struck with a club. Softer cover materials such as balata and softer ionomers in some instances, have been employed in two piece construction balls in order to provide improved "feel" and increased spin rates.

Wound balls typically have either a solid rubber or liquid filled center around which many yards of a stretched elastic thread or yarn are wound to form a core. The wound core is then covered with a durable cover material such as a SURLYN® or similar material or a softer cover such as balata. Wound balls are generally softer than two piece balls and provide more spin, which enables a skilled golfer to have more control over the ball's flight. In particular, it is desirable that a golfer be able to impart back spin to a golf ball for purposes of controlling its flight and controlling the action of the ball upon landing on the ground. For example, substantial back spin will make the ball stop once it strikes the landing surface instead of bounding forward. The ability to impart back spin onto a golf ball is related to the extent to which the golf ball cover deforms when it is struck with a golf club. Because wound balls are traditionally more deformable than conventional two piece balls, it is easier to impart spin to wound balls. However, wound higher spinning balls typically travel a shorter distance when struck as

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compared to a two piece ball. Moreover, as a result of their more complex structure, wound balls generally require a longer time to manufacture and are more expensive to produce than a two piece ball.

The United States Golf Association (USGA) has instituted a rule that prohibits the competitive use in any USGA sanctioned event of a golf ball that can achieve an initial velocity of greater than 76.2 meters per second (m/s), or 250 ft/s, when struck by a driver with a velocity of 39.6 m/s, i.e., 130 ft/s (referred to hereinafter as "the USGA test"). However, an allowed tolerance of two percent permits manufacturers to produce golf balls that achieve an initial velocity of 77.7 m/s (255 ft/s).

Regardless of the form of the ball, players generally seek a golf ball that delivers maximum distance, which requires a high initial velocity upon impact. Therefore, in an effort to meet the demands of the marketplace, manufacturers strive to produce golf balls with initial velocities in the USGA test that approximate the USGA maximum of 77.7 m/s or 255 ft/s as closely as possible.

Therefore, golf ball manufacturers are continually searching for new ways in which to provide golf balls that deliver the maximum performance in terms of both distance and spin rate for golfers of all skill levels.

Relatively recently, a number of golf ball manufacturers have introduced multilayer golf balls, i.e., having multiple core intermediate mantle and/or cover layers, in an effort to overcome some of the undesirable aspects of conventional two piece balls, such as their hard feel, while maintaining the positive attributes of these golf balls (including their increased initial velocity and distance). Examples of multilayer balls include the Altus Newing (Bridgestone), Reygrande 2x2, Giga (Spalding) Metal Mix (Dunlop), Ultra Tour Balata (Wilson).

Additionally, a number of patents have been issued directed towards modifying the properties of a conventional two piece ball by altering the typical single layer core and/or single cover layer construction to provide a multilayer core and/or cover. The inventions disclosed in these patents are directed towards improving a variety of golf ball characteristics.

For example, there are a number of multilayer ball patents directed towards improving the spin, click or feel of solid balls while maintaining the distance provided by the solid construction. A variety of approaches to manipulating the core construction are described in the art. For example, U.S. Pat. No. 5,072,944 discloses a three-piece solid golf ball having a center and outer layer which are prepared from a rubber composition, preferably having a base rubber of polybutadiene. This patent teaches that it is desirable that the center core is softer than the outer layer, wherein the layers have a hardness (Shore C) of 25-50 and 70-90 respectively.

U.S. Pat. No. 4,625,964 relates to a solid golf ball having a polybutadiene rubber core of a diameter not more than 32 mm, and a polybutadiene rubber intermediate layer having a specific gravity lower than that of the core material.

U.S. Pat. No. 4,848,770 discloses a non-wound three-piece golf ball which includes a core of a highly filled synthetic rubber or polymeric material, an intermediate mantle of an unfilled synthetic rubber and a cover. The core and intermediate mantle have a hardness between 50-95.

U.S. Pat. No. 5,002,281 is directed towards a three-piece solid golf ball which has an inner core having a hardness of 25-70 (Shore C) and an outer shell having a hardness of 80-95 (Shore C), wherein the specific gravity of the inner core must be greater than 1.0, but less than or equal to that of the outer shell, which must be less than 1.3.

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U.S. Pat. No. 5,253,871 concerns a golf ball having a three piece structure comprising an elastomer core, an intermediate layer of a thermoplastic material containing at least 10% of ether block copolymer, preferably blended with an ionomer and a thermoplastic cover.

Several additional patents are directed to golf balls having multiple cover layers. For example U.S. Pat. No. 4,431,193 relates to a golf ball having a multilayer cover wherein the inner layer is a hard, high flexural modulus ionomer resin and the outer layer is a soft, low flexural modulus ionomer resin, wherein either or both layers may comprise a foamed ionomer resin.

U.S. Pat. No. 5,314,187 also relates to golf balls having a cover formed with multiple layers, wherein the outer layer is molded over the inner layer and comprises a blend of balata and an elastomer and the inner layer is an ionomer resin.

U.S. Pat. No. 4,919,434 is directed towards a golf ball having a cover which comprises an inner layer and an outer layer each of which comprise a thermoplastic resin, preferably the layers comprise of materials that are capable of fusion bonding with each other.

UK Patent Application Nos. GB 2,291,817 and 2,291,812 are both directed towards a wound golf ball with improved distance comprising a dual cover layer, wherein the inner cover layer has a high hardness as compared to the outer cover layer. These references teach that the cover layers may be formed from balata or ionomer resins and should have a combined thickness of less than 4 mm.

UK Patent Application No. GB 2,278,609 discloses a multilayer golf ball providing enhanced distance without sacrificing playability or durability comprising a core, an inner cover layer and an outer cover layer wherein the inner cover layer comprises a high acid ionomer and the outer cover layer comprises a soft ionomer or a non-ionic thermoplastic elastomer.

However, none of these patents disclose a multilayer ball having a very thin thermoset outer layer formed from a castable reactive liquid as disclosed herein to provide golf balls exhibiting a "progressive performance" such as those golf balls of the present invention.

SUMMARY OF THE INVENTION

The present invention is directed towards a multilayer golf ball which provides "progressive performance" characteristics when struck with golf clubs of varying head speeds and loft angles.

The present invention is further directed towards a multilayer golf ball which in general comprises a core, an inner cover layer and a very thin (i.e., <0.05") outer cover layer, wherein the inner cover layer comprises a high flexural modulus material and the outer cover layer comprises a thermoset material which is formed from a castable reactive liquid material.

In one particular embodiment, the present invention is directed towards a multilayer golf ball which comprises a core, an inner cover layer and a very thin outer cover layer, wherein: a) the core comprises a solid or liquid filled center around which a length of elastic thread is wound; b) the inner cover layer comprises a high flexural modulus material; and c) the outer cover layer comprises a thermoset material which is formed from a castable reactive liquid.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a cross-section of a golf ball 2 having a core 4, an inner cover layer 6 and an outer cover layer 8.

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DETAILED DESCRIPTION OF THE INVENTION

By the present invention, it has been discovered that a golf ball of the presently claimed construction has a "progressive performance" when struck with a variety of clubs. More specifically, as used herein, the term "progressive performance" means that the presently claimed golf ball has the distance benefits of a traditional hard covered two piece ball when struck with a club having a high club head speed and a low loft angle, but also the high spin and feel characteristics similar to that of a traditional soft covered wound ball when struck with a club having a low head speed and high loft angle. Thus, golf balls of the presently claimed construction provide the "best of both worlds" in the golf ball art, i.e., a maximum distance ball for long shots (e.g., with a driver) which has high spin and controllability for short shots (e.g., with a wedge).

Without being limited to any particular theory, it is believed that with low club head speed and high loft shots such as those made with an 8-iron or a wedge, a ball's surface hardness has a greater influence on the ball's flight characteristics than the ball's overall construction. Thus, all other parameters being equal, a ball with a softer surface will have a higher spin rate than one with a harder surface, regardless of the ball's overall construction. Conversely, however, when a golf ball is struck with a high club head speed and a low loft angle, such as that of a driver, it appears that the opposite is true and that the overall construction of the ball has a greater influence on the ball's flight characteristics than does the surface hardness.

Accordingly, by the present invention, it has been found that by creating a golf ball with a low spin construction, but adding a very thin layer of a relatively soft thermoset material formed from a castable reactive liquid, a golf ball with "progressive performance" from driver to wedge can be formed. As used herein, the term "thermoset" material refers to an irreversible, solid polymer that is the product of the reaction of two or more prepolymer precursor materials.

The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer and an outer cover layer. The thickness of the outer cover layer is critical to the "progressive performance" of the golf balls of the present invention. If the outer cover layer is too thick, this cover layer will contribute to the in-flight characteristics related to the overall construction of the ball and not the cover surface properties. However, if the outer cover layer is too thin, it will not be durable enough to withstand repeated impacts by the golfer's clubs. Specifically, it has been determined that the outer cover layer must have a thickness of less than about 0.05 inches, preferably between about 0.02 and about 0.04 inches. Most preferably, this thickness is about 0.03 inches.

The outer cover layer is formed from a relatively soft thermoset material in order to replicate the soft feel and high spin play characteristics of a balata ball when the balls of the present invention are used for pitch and other "short game" shots. In particular, the outer cover layer should have a Shore D hardness of from about 30 to about 60, preferably 35-50 and most preferably 40-45. Additionally, the materials of the outer cover layer must have a degree of abrasion resistance in order to be suitable for use as a golf ball cover.

The outer cover layer of the present invention can comprise any suitable thermoset material which is formed from a castable reactive liquid material. The preferred materials for the outer cover layer include, but are not limited to, thermoset urethanes and polyurethanes, thermoset urethane

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ionomers and thermoset urethane epoxies. Examples of suitable polyurethane ionomers are disclosed in co-pending U.S. patent application Ser. No. 08/482,519, filed Jun. 7, 1995, entitled "Golf Ball Covers", the disclosure of which is hereby incorporated by reference in its entirety in the present application.

Thermoset polyurethanes and urethanes are particularly preferred for the outer cover layers of the balls of the present invention. Polyurethane is a product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agent is typically either a diamine or glycol. Often a catalyst is employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Conventionally, thermoset polyurethanes are prepared using a diisocyanate, such as 2,4-toluene diisocyanate (TDI) or methylenebis(4-cyclohexyl isocyanate) (HMDI) and a polyol which is cured with a polyamine, such as methylenedianiline (MDA), or a trifunctional glycol, such as trimethylol propane, or tetrafunctional glycol, such as N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine. However, the present invention is not limited to just these specific types of thermoset polyurethanes. Quite to the contrary, any suitable thermoset polyurethane may be employed to form the outer cover layer of the present invention.

The inner cover layer of the present invention is formed from a hard, high flexural modulus, resilient material which contributes to the low spin, distance characteristics of the presently claimed balls when they are struck for long shots (e.g. driver or long irons). Specifically, the inner cover layer materials have a Shore D hardness of about 65–80, preferably about 69–74 and most preferably about 70–72. Furthermore, as defined herein, the term "high flexural modulus" means a flexural modulus (as measured by ASTM 790) of at least about 65,000 psi, preferably about 70,000 psi to about 120,000 psi and most preferably at least about 75,000 psi. The thickness of the inner cover layer can range from about 0.020 inches to about 0.045 inches, preferably about 0.030 inches to about 0.040 inches and most preferably about 0.035 inches.

The inner cover layer may be formed from a wide variety of hard, high flexural modulus resilient materials. Among the preferred inner cover materials are hard, high flexural modulus ionomer resins and blends thereof. These ionomers are obtained by providing a cross metallic bond to polymers of monoolefin with at least one member selected from the group consisting of unsaturated mono- or di-carboxylic acids having 3 to 12 carbon atoms and esters thereof (the polymer contains 1 to 50% by weight of the unsaturated mono- or di-carboxylic acid and/or ester thereof). More particularly, such acid-containing ethylene copolymer ionomer component includes E/X/Y copolymers where E is ethylene, X is a softening comonomer such as acrylate or methacrylate present in 0–50 (preferably 0–25, most preferably 0–20), weight percent of the polymer, and Y is acrylic or methacrylic acid present in 5–35 (preferably at least about 16, more preferably at least about 16–35, most preferably at least about 16–20) weight percent of the polymer, wherein the acid moiety is neutralized 1–90% (preferably at least 40%, most preferably at least about 60%) to form an ionomer by a cation such as lithium*, sodium*, potassium, magnesium*, calcium, barium, lead, tin, zinc* or aluminum (*=preferred), or a combination of such cations. Specific acid-containing ethylene copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl

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acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/ethyl acrylate, and ethylene/(meth)acrylic acid/methyl acrylate copolymers.

The manner in which the ionomers are made is well known in the art as described in e.g., U.S. Pat. No. 3,262, 272. Such ionomer resins are commercially available from DuPont Co. under the tradename SURLYN® and from Exxon under the tradename Iotek®. Some particularly suitable SURLYN® include SURLYN® 8140 (Na) and SURLYN® 8546 (Li) which have a methacrylic acid content of about 19%.

However, the materials for the inner cover layer are not limited to ionomer resins. Instead, the present invention contemplates that virtually any hard, high flexural modulus, resilient material which is compatible with the other materials of the golf ball may be employed as the inner cover layer. Examples of other suitable inner cover materials include thermoplastic or thermoset polyurethanes, thermoplastic or thermoset polyetheresters or polyetheramides, thermoplastic or thermoset polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer or blends thereof.

Suitable thermoplastic polyetheresters include materials which are commercially available from DuPont under the tradename Hytrel®. Suitable thermoplastic polyetheramides include materials which are available from Elf-Atochem under the tradename Pebax®. Other suitable materials for the inner cover layer include nylon and acrylonitrile-butadiene-styrene copolymer (ABS).

The golf ball cores of the present invention may comprise any of a variety of constructions. For example, the core of the golf ball may comprise a conventional center surrounded by an intermediate mantle layer disposed between the center and the inner cover layer. The core may be a single layer or may comprise a plurality of layers. The innermost portion of the core may be solid or it may be a liquid filled sphere. As with the core, the intermediate mantle layer may also comprise a plurality of layers. The core may also comprise a solid or liquid filled center around which many yards of a stretched elastic thread or yarn are wound.

The materials for solid cores include compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking or initiator agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt of an unsaturated fatty acid such as a zinc salt or a magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms such as

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acrylic or methacrylic acid. Suitable cross linking agents include metal salt diacrylates, dimethacrylates and monomethacrylates wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium or nickel.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include peroxide compounds such as dicumyl peroxide, 1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane, a-a bis (t-butylperoxy) diisopropylbenzene, 2,5-dimethyl-2,5 di(t-butylperoxy) hexane or di-t-butyl peroxide and mixtures thereof.

Conventional prior art golf balls typically incorporate 5 to 50 pph of zinc oxide in a diacrylateperoxide core system. However, the zinc oxide may be replaced by calcium oxide in a diacrylate-peroxide system to provide a suitable core composition.

As used herein, the term "filler" includes any compound or composition that can be used to vary the density and other properties of the core. Fillers typically includes materials such as zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate reground (recycled core material ground to 30 mesh particle) and the like.

In one embodiment of the present invention, the core comprises a center which is liquid-filled or solid around which an elastic thread is wound. The solid center is typically a homogenous mass of a resilient material such as polybutadiene or a natural rubber. The liquid-filled center is typically a thin walled sphere made from a thermoplastic or thermoset material into which a liquid such as corn syrup is injected by means of a needle. The sphere is then sealed and typically frozen to make the core a solid mass. The windings for either type of center are provided by an elastic thread which is stretched and wound about the core to a desired thickness.

The overall outer diameter (OD) of the core (including the center and any intermediate mantle layer(s) or windings) together with the inner cover layer of the golf balls of the present invention is about 1.580 inches to about 1.640 inches, preferably about 1.60 inches to about 1.630 inches, and most preferably about 1.620 inches.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association (USGA) specifications limit the minimum size of a competition golf ball to more than 1.680 inches in diameter, there is no specification as to the maximum diameter. Moreover, golf balls of any size can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

The cores and inner cover of the golf balls of the present invention can be made by any conventional process employed in the golf ball art. For example, the solid centers can be either injection or compression molded. Similarly, the wound centers employed in the present invention can be produced through conventional means. The inner cover layer and any mantle layer(s) are subsequently injection or compression molded about the core.

However, due to the very thin nature (less than 0.05"), it is not practical to form the outer cover layers of the ball of the present invention using conventional injection or compression molding techniques ordinarily employed in the golf ball art for applying cover materials. These conventional ball molding processes are not capable of easily applying such thin outer cover layers over a solid spherical surface.

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Accordingly, it has been found by the present invention that the use of a castable, reactive material which is applied in a fluid form makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids which react to form a thermoset material provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the thermoset material can be applied over the inner core using a variety of application techniques such as spraying, dipping, spin coating or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in co-pending U.S. patent application Ser. No. 08/432,657, filed May 2, 1995 entitled "Method And Apparatus For Forming Polyurethane Cover On A Golf Ball", the disclosure of which is hereby incorporated by reference in its entirety in the present application. Similarly, U.S. Pat. No. 5,006,297 to Brown et al. and U.S. Pat. No. 5,334,673 to Wu both also disclose suitable coating techniques which may be utilized to apply the castable reactive liquids employed in the present invention. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

The following example of multilayer golf balls formed according to the present invention is given to illustrate the present invention. However, it is to be understood that the example is for illustrative purposes only and in no manner is the present invention limited to the specific disclosures therein.

EXAMPLE 1

Golf balls of the present invention can be manufactured as follows. The core may be made using either a conventional wound core construction or a conventional twopiece core construction formed using methods well known in the art. The wound core construction can be either a solid rubber-based center or a liquid filled center around which a length of elastic thread is wound. A conventional two-piece construction preferably comprises a cis 1,4 polybutadiene rubber that has been crosslinked with a metal salt of an unsaturated fatty acid such as zinc diacrylate.

These core constructions are then covered using a conventional compression molding technique with an inner cover layer of an ionomer having a methacrylic acid content of at least about 16 weight percent (preferably SURLYN 8140 or SURLYN 8546).

The outer cover layer can be formed following the processes set forth in U.S. Pat. No. 5,006,297 and U.S. Pat. No. 5,334,673. A particularly desired material for forming the outer cover layer is 40D castable urethane.

It is believed that golf balls made in accordance with the present invention will exhibit an appreciably lower spin rate when struck with a driver (and thus a greater overall distance) as compared to conventional "high performance" golf balls (e.g. Tour Balata [Titleist]), but have very similar or even higher spin rates when struck with an 8 iron and/or a "50 yard" wedge, thereby evidencing a "progressive performance" from driver to wedge in the golf balls of the present invention.

While it is apparent that the illustrative embodiments of the invention herein discloses fulfills the objective stated above, it will be appreciated that numerous modifications and other embodiments may be devised by those skilled in the art. Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments which come within the spirit and scope of the present invention.

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We claim:

1. A golf ball comprising a cover and a core, wherein said cover is disposed about the core and said cover comprises:

- (a) an inner cover layer of a flexural modulus of at least about 65,000 psi; and
 - (b) an outer cover layer having a Shore D hardness of greater than 30 to 60, having a thickness of less than 0.050 inches and comprising a thermoset material that includes at least one of a castable reactive liquid material and reaction products thereof.
2. The golf ball of claim 1, wherein the outer layer has a Shore D hardness of less than 60.
3. The golf ball of claim 1, wherein the outer layer has a Shore D hardness of between 35 to 50.
4. The golf ball of claim 3, wherein the inner layer has a flexural modulus of from 70,000 to 120,000 psi.
5. The golf ball of claim 4, wherein the inner layer has a Shore D hardness of 69 to 74.
6. The golf ball of claim 1, wherein the inner layer has a Shore D hardness of at least 65.
7. The golf ball of claim 1, wherein the thermoset material comprises a material selected from the group consisting of a polyurethane, a urethane ionomer and a urethane epoxy.
8. The golf ball of claim 1 wherein the inner cover layer comprises an ionomer resin, a polyurethane, a polyetherester, a polyetheramide, a polyester, a dynamically vulcanized elastomer, a functionalized styrenebutadiene elastomer, a metallocene polymer nylon, acrylonitrile butadiene-styrene copolymer or blends thereof.
9. The golf ball of claim 8, wherein the inner cover layer comprises an ionomer resin which comprises at least 16 wt. percent of carboxylic acid.
10. The golf ball of claim 1, wherein the outer diameter of the core and the inner cover layer is less than 1.640 inches.

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11. A golf ball comprising a cover and a core, wherein:

- (a) the cover comprises an inner cover layer and an outer cover layer;
 - (b) said inner cover layer comprises an ionomer resin having a flexural modulus of at least 65,000 psi;
 - (c) said outer cover layer has a thickness of 0.02 inches to 0.045 inches and comprises a polyurethane formed from a castable, reactive liquid material.
12. The golf ball of claim 11, wherein the core comprises a liquid filled center.
13. The golf ball of claim 12, wherein the core comprises a center around which a length of elastic thread is wound.
14. The golf ball of claim 13, wherein the inner cover layer comprises an ionomer.
15. A golf ball comprising a cover and a core, wherein:
- (a) the cover comprises an inner cover layer and an outer cover layer;
 - (b) said inner cover layer comprises an ionomer having a flexural modulus of at least 65,000 psi and a thickness of 0.035 inches; and
 - (c) said outer cover layer has a thickness of 0.030 inches and comprises a polyurethane formed from a castable, reactive liquid.
16. The golf ball of claim 15, wherein the core comprises a solid sphere.
17. The golf ball of claim 15, wherein the core comprises a solid center around which a length of elastic thread is wound.
18. The golf ball of claim 15, wherein the core comprises a liquid filled center around which a length of elastic thread is wound.

* * * * *

**DECLARATION OF THOMAS L. HALKOWSKI
IN SUPPORT OF CALLAWAY GOLF'S
MOTION *IN LIMINE* TO EXCLUDE
ACUSHNET'S "TEST BALLS" AND RELATED
TESTIMONY**

EXHIBIT 2



US005820489A

United States Patent [19]

Sullivan et al.

[11] **Patent Number:** 5,820,489[45] **Date of Patent:** *Oct. 13, 1998[54] **LOW SPIN GOLF BALL**[75] Inventors: **Michael J. Sullivan**, Chicopee; **R. Dennis Nesbitt**, Westfield, both of Mass.[73] Assignee: **Lisco, Inc.**, Tampa, Fla.

[*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. No. 5,368,304.

[21] Appl. No.: **716,016**[22] Filed: **Sep. 19, 1996****Related U.S. Application Data**

[62] Division of Ser. No. 255,442, Jun. 8, 1994, abandoned, Continuation of Ser. No. 54,406, Apr. 28, 1993, Pat. No. 5,368,304.

[51] Int. Cl.⁶ **A63B 37/06; A63B 37/12**[52] U.S. Cl. **473/377; 273/DIG. 20; 273/DIG. 22**[58] Field of Search **473/377, DIG. 20, 473/DIG. 22**[56] **References Cited****U.S. PATENT DOCUMENTS**

5,368,304 11/1994 Sullivan et al. 473/377

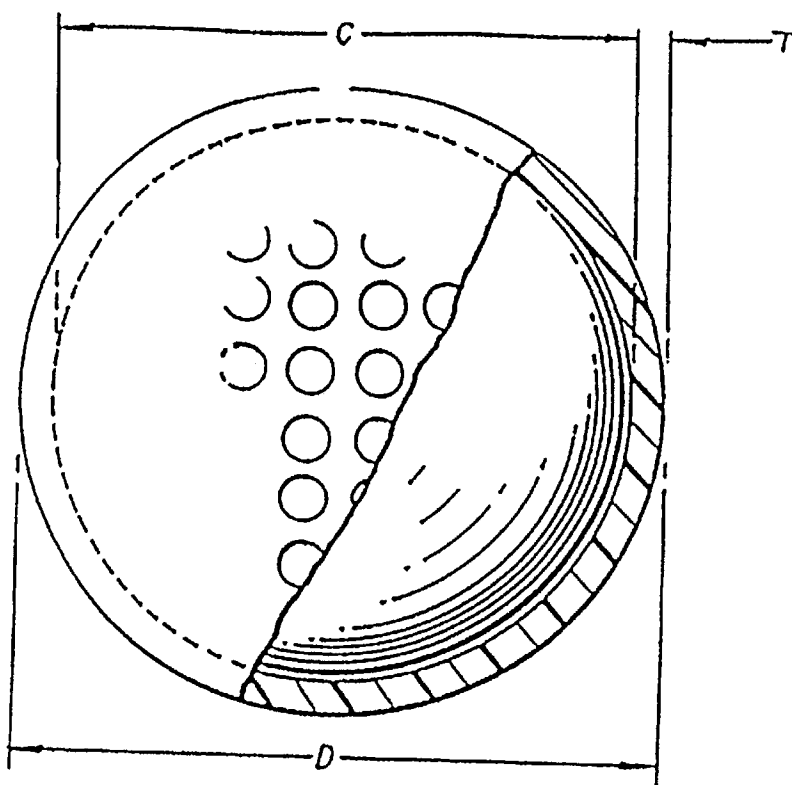
5,580,057 12/1996 Sullivan et al. 473/377

Primary Examiner—George J. Marlo*Attorney, Agent, or Firm*—Fay, Sharpe, Beall, Fagan, Minnich & McKee[57] **ABSTRACT**

A golf ball comprising:

a core comprising a diene polymer having a Riehle compression of at least 0.075; and

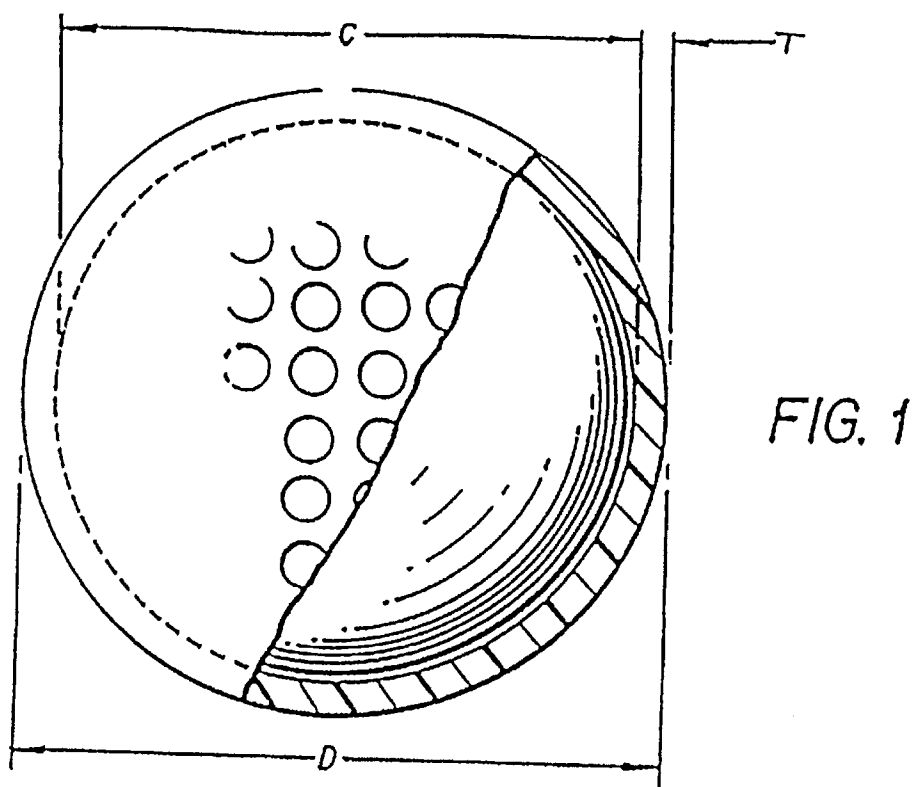
a cover having a Shore D hardness of at least 65, wherein the cover is comprised of at least one high acid ionomer resin comprising a copolymer of greater than 16% by weight of an alpha, beta-unsaturated carboxylic acid, and an alpha olefin of which about 10 to about 90% of the carboxyl groups of the copolymer are neutralized with a metal cation. The golf ball has a diameter of 1.700–1.800 inches. The thickness of the cover is in the range of 0.08 to 0.13 inches.

13 Claims, 1 Drawing Sheet

U.S. Patent

Oct. 13, 1998

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LOW SPIN GOLF BALL

This is a divisional of application Ser. No. 08/255,442 filed on Jun. 8, 1994, now abandoned, which in turn is a continuation of U.S. application Ser. No. 08/054,406 filed on Apr. 28, 1993 now U.S. Pat. No. 5,368,304 filed Nov. 29, 1994.

FIELD OF THE INVENTION

The present invention relates to golf balls and, more particularly, to improved two-piece golf balls having low spin rates. The improvement in the golf balls results from a combination of a softened polybutadiene core and a hard cover made from blends of one or more specific hard, high stiffness ionomers. The combination of a soft core and a hard cover leads to an improved golf ball having a lower than anticipated spin rate while maintaining the resilience and durability characteristics necessary for repetitive play.

In an additional embodiment of the invention, the spin rate is further reduced by decreasing the weight of the softened polybutadiene core while maintaining core size and by increasing the thickness of the cover. The larger, less dense finished ball exhibits lower spin rates after club impact than conventional balls.

BACKGROUND OF THE INVENTION

Spin rate is an important golf ball characteristic for both the skilled and unskilled golfer. High spin rates allow for the more skilled golfer, such as PGA professionals and low handicap players, to maximize control of the golf ball. This is particularly beneficial to the more skilled golfer when hitting an approach shot to a green. The ability to intentionally produce "back spin", thereby stopping the ball quickly on the green, and/or "side spin" to draw or fade the ball, substantially improves the golfer's control over the ball. Thus, the more skilled golfer generally prefers a golf ball exhibiting high spin rate properties.

However, a high spin golf ball is not desirous by all golfers, particularly high handicap players who cannot intentionally control the spin of the ball. In this regard, less skilled golfers, have, among others, two substantial obstacles to improving their game: slicing and hooking. When a club head meets the ball, an unintentional side spin is often imparted which sends the ball off its intended course. The side spin reduces one's control over the ball as well as the distance the ball will travel. As a result, unwanted strokes are added to the game.

Consequently, while the more skilled golfer desires a high spin golf ball, a more efficient ball for the less skilled player is a golf ball that exhibits low spin properties. The low spin ball reduces slicing and hooking and enhances roll distance for the amateur golfer.

The present inventors have addressed the need for developing a golf ball having a reduced spin rate after club impact, while at the same time maintaining durability, playability and resiliency characteristics needed for repeated use. The reduced spin rate golf ball of the present invention meets the rules and regulations established by the United States Golf Association (U.S.G.A.).

Along these lines, the U.S.G.A. has set forth five (5) specific regulations that a golf ball must conform to. The U.S.G.A. rules require that a ball be no smaller than 1.680 inches in diameter. However, notwithstanding this restriction, there is no specific limitation as to the maximum permissible diameter of a golf ball. As a result, a golf ball

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can be as large as desired so long as it is larger than 1.680 inches in diameter and so long as the other four (4) specific regulations are met.

The U.S.G.A. rules also require that balls weigh no more than 1.620 ounces, and that their initial velocity may not exceed 250 feet per second with a maximum tolerance of 2%, or up to 255 ft./sec. Further, the U.S.G.A. rules state that a ball may not travel a distance greater than 280 yards with a test tolerance of 6% when hit by the U.S.G.A. outdoor driving machine under specific conditions.

It has been determined by the present inventors that the combination of a relatively soft core (i.e. Riehle compression of about 0.075 to 0.115) and a hard cover (i.e. Shore D hardness of 65 or more) significantly reduces the overall spin rate of the resulting two piece golf ball. The inventors have also learned that an increase in cover thickness, thereby increasing the overall diameter of the resulting molded golf ball, further reduces spin rate.

Top-grade golf balls sold in the United States may be generally classified as one of two types: two-piece or three-piece balls. The two-piece ball, exemplified by the balls sold by Spalding & Evenflo Companies, Inc. (the assignee of the present invention through its wholly owned subsidiary, Lisco, Inc.) under the trademark TOP-FLITE, consists of a solid polymeric core and a separately formed outer cover. The so-called three-piece balls, exemplified by the balls sold under the trademark TITLEIST by the Acushnet Company, consist of a liquid (e.g., TITLEIST TOUR 384) or solid (e.g., TITLEIST DT) center, elastomeric thread windings about the center, and a cover.

Spalding's two-piece golf balls are produced by molding a natural (balata) or synthetic (i.e. thermoplastic resin such as an ionomer resin) polymeric cover composition around a preformed polybutadiene (rubber) core. During the molding process, the desired dimple pattern is molded into the cover material. In order to reduce the number of coating steps involved in the finishing of the golf balls, a color pigment or dye and, in many instances, an optical brightener, are added directly to the generally "off white" colored polymeric cover composition prior to molding. By incorporating the pigment and/or optical brightener in the cover composition molded onto the golf ball core, this process eliminates the need for a supplemented pigmented painting step in order to produce a white or colored (notably orange, pink and yellow) golf ball.

With respect to multi-layered golf balls, Spalding is the leading manufacturer of two-piece golf balls in the world. Spalding manufactures over sixty (60) different types of two-piece balls which vary distinctly in such properties as playability (i.e. spin rate, compression, feel, etc.), travel distance (initial velocity, C.O.R., etc.), durability (impact, cut and weather resistance) and appearance (i.e. whiteness, reflectance, yellowness, etc.) depending upon the ball's core, cover and coating materials, as well as the ball's surface configuration (i.e. dimple pattern). Consequently, Spalding's two-piece golf balls offer both the amateur and professional golfer a variety of performance characteristics to suit an individual's game.

In regard to the specific components of a golf ball, although the nature of the cover can, in certain instances, make a significant contribution to the overall feel, spin (control), coefficient of restitution (C.O.R.) and initial velocity of a ball (see, for example, U.S. Pat. No. 3,819,768 to Molitor), the initial velocity of two-piece and three-piece balls is determined mainly by the coefficient of restitution of the core. The coefficient of restitution of the core of wound

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(i.e. three-piece) balls can be controlled within limits by regulating the winding tension and the thread and center composition. With respect to two-piece balls, the coefficient of restitution of the core is a function of the properties of the elastomer composition from which it is made.

The cover component of a golf ball is particularly influential in effecting the compression (feel), spin rates (control), distance (C.O.R.), and durability (i.e. impact resistance, etc.) of the resulting ball. Various cover compositions have been developed by Spalding and others in order to optimize the desired properties of the resulting golf balls.

Over the last twenty (20) years, improvements in cover and core material formulations and changes in dimple patterns have more or less continually improved golf ball distance. Top-grade golf balls, however, must meet several other important design criteria. To successfully compete in today's golf ball market, a golf ball should be resistant to cutting and must be finished well; it should hold a line in putting and should have good click and feel. In addition, the ball should exhibit spin and control properties dictated by the skill and experience of the end user.

The present invention is directed to improved top-grade golf balls having reduced spin rates. The improved golf balls offer the less skilled golfer better control over his or her shots and allow for greater distance.

In an alternative embodiment, the spin rate of the ball is further reduced by increasing the thickness of the cover and/or decreasing the weight and softness of the core. By increasing the cover thickness and/or the overall diameter of the resulting molded golf ball, enhanced reduction in spin rate is observed.

With respect to the increased size of the ball, over the years golf ball manufacturers have generally produced golf balls at or around the minimum size and maximum weight specifications set forth by the U.S.G.A. There have, however, been exceptions, particularly in connection with the manufacture of golf balls for teaching aids. For example, oversized, overweight (and thus unauthorized) golf balls have been on sale for use as golf teaching aids (see U.S. Pat. No. 3,201,384 to Barber).

Oversized golf balls are also disclosed in New Zealand Patent 192,618 dated Jan. 1, 1980, issued to a predecessor of the present assignee. This patent teaches an oversize golf ball having a diameter between 1.700 and 1.730 inches and an oversized core of resilient material (i.e. about 1.585 to 1.595 inches in diameter) so as to increase the coefficient of restitution.

Additionally, the patent discloses that the ball should include a cover having a thickness less than the cover thickness of conventional balls (i.e. a cover thickness of about 0.050 inches as opposed to 0.090 inches for conventional two-piece balls).

In addition, it is also noted that golf balls made by Spalding in 1915 were of a diameter ranging from 1.630 inches to 1.710 inches. As the diameter of the ball increased, the weight of the ball also increased. These balls were comprised of covers made up of balata/gutta percha and cores made from solid rubber or liquid sacs and wound with elastic thread.

Golf balls known as the LYNX JUMBO were also commercially available by Lynx in October, 1979. These balls had a diameter of 1.76 to 1.80 inches. It met with little or no commercial success. The LYNX JUMBO balls consisted of a core comprised of wound core and a cover comprised of natural or synthetic balata.

However, notwithstanding the enhanced diameters of these golf balls, none of these balls produced the enhanced

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spin reduction characteristics and overall playability, distance and durability properties of the present invention and/or fall within the regulations set forth by the U.S.G.A. An object of the present invention is to produce a U.S.G.A. regulation golf ball having improved low spin properties while maintaining the resilience and durability characteristics necessary for repetitive play.

These and other objects and features of the invention will be apparent from the following summary and description of the invention and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The following is a brief description of the drawings which are presented for the purposes of illustrating the invention and not for purposes of limiting the same.

FIG. 1 illustrates a partially broken-away view of the improved golf ball of the present invention wherein D is the diameter of the ball; C is the diameter of the core and T is the thickness of the cover.

SUMMARY OF THE INVENTION

The present invention is directed to improved golf balls having a low rate of spin upon club impact. The golf balls comprise a soft polybutadiene core and a hard cover. The hard cover is preferably sized to be larger than conventional diameters. The low spin rate enables the ball to travel a greater distance. In addition, the low spin rate provides the less skilled golfer with more control. This is because the low spin rate decreases undesirable side spin which leads to slicing and hooking. The combination of a hard cover and a soft core provides for a ball having a lower than anticipated spin rate while maintaining high resilience and good durability.

The golf ball comprises a core and a cover. The core has a Rieble compression of at least 0.075, preferably 0.075 to about 0.115, and a PGA compression of about 45 to 85. The cover has a Shore D hardness of at least 65.

In an alternative embodiment, the resulting ball is larger than the standard 1.680 inch golf ball. Its diameter is in the range of about 1.680 to 1.800 inches, more likely in the range of about 1.700 to 1.800 inches, preferably in the range of 1.710–1.730 inches, and most preferably in the range of about 1.717–1.720 inches. The larger diameter of the golf ball (see FIG. 1) results from the cover thickness which ranges from more than the standard 0.0675 inches up to about 0.130, preferably from about 0.0675 to about 0.1275 inches, more preferably in the range of about 0.0825 to 0.0925, and most preferably in the range of about 0.0860 to 0.0890 inches. The core is of a standard size, roughly about 1.540 to 1.545 inches.

The core used in the present invention is a specially produced softened polybutadiene elastomeric solid core having a conventional diameter of about 1.540 to 1.545 inches. The core is produced from a composition comprising a base elastomer selected from polybutadiene and mixtures of polybutadiene with other elastomers, at least one metallic salt of an unsaturated carboxylic acid (a co-crosslinking agent), and free radical initiator (a co-crosslinking agent). In addition, a suitable and compatible modifying ingredient including, but not limited to metal activators, fatty acids, fillers, polypropylene powder and other additives may be included.

Of particular concern, only a limited amount of the metallic salt of an unsaturated carboxylic acid is included in the core compositions in order to produce the degree of core

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softness and weight desired. In this regard, it is understood that when a larger overall ball is desired, the composition of the core is adjusted so that the molded finished ball falls within the weight parameters set forth by the U.S.G.A. Since the finished golf balls must still meet the U.S.G.A. weight limitation of 1.620 ounces, the core component of the larger and thicker covered balls are designed to be not only softer, but also lighter in weight.

In such circumstances, the specific gravity of the core is less than that of a standard core since the larger ball must weigh the same as a standard ball. The core generally weighs about 36 to 37 grams for an standard sized finished ball and about 33 to 34 grams for an oversized finished ball.

The core composition produces a softer molded core which still maintains the resilience (C.O.R.), compression (hardness) and durability characteristics required. The overall molded core has a PGA compression of about 45 to 85, preferably in the range of about 70-80. Its Riehle compression is about 0.075 or more, preferably in the range of 0.075 to 0.115, and the resilience of the core is about 0.760 to 0.780.

The cover is preferably comprised of a hard, high-stiffness ionomer resin, most preferably a metal cation neutralized high acid ionomer resin containing more than 16% carboxylic acid by weight, or blend thereof. The cover has a Shore D hardness of about 65 or greater.

With respect to the ionomeric cover composition of the invention, ionomeric resins are polymers containing inter-chain ionic bonding. As a result of their toughness, durability, and flight characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under the trademark "Surllyn®" and more recently, by the Exxon Corporation (see U.S. Pat. No. 4,911,451) under the trademark "Escor®" and the tradename "Iotek", have become the materials of choice for the construction of golf ball covers over the traditional "balata" (trans-polyisoprene, natural or synthetic) rubbers.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid or maleic acid. In some instances, an additional softening comonomer such as an acrylate can also be included to form a terpolymer. The pendent ionic groups in the ionomeric resins interact to form ion-rich aggregates contained in a non-polar polymer matrix. The metal ions, such as sodium, zinc, magnesium, lithium, potassium, calcium, etc. are used to neutralize some portion of the acid groups in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e., improved durability, etc. for golf ball construction over balata.

The ionomeric resins utilized to produce cover compositions can be formulated according to known procedures such as those set forth in U.S. Pat. No. 3,421,766 or British Patent No. 963,380, with neutralization effected according to procedures disclosed in Canadian Patent Nos. 674,595 and 713,631, wherein the ionomer is produced by copolymerizing the olefin and carboxylic acid to produce a copolymer having the acid units randomly distributed along the polymer chain. Broadly, the ionic copolymer generally comprises one or more α -olefins and from about 9 to about 20 weight percent of α , β -ethylenically unsaturated mono- or dicarboxylic acid, the basic copolymer neutralized with metal ions to the extent desired.

At least about 20% of the carboxylic acid groups of the copolymer are neutralized by the metal ions (such as sodium, potassium, zinc, calcium, magnesium, and the like)

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and exist in the ionic state. Suitable olefins for use in preparing the ionomeric resins include ethylene, propylene, butene-1, hexene-1 and the like. Unsaturated carboxylic acids include acrylic, methacrylic, ethacrylic, α -chloroacrylic, crotonic, maleic, fumaric, itaconic acids, and the like. The ionomeric resins utilized in the golf ball industry are generally copolymers of ethylene with acrylic (i.e., Escor®) and/or methacrylic (i.e., Surllyn®) acid. In addition, two or more types of ionomeric resins may be blended in to the cover compositions in order to produce the desired properties of the resulting golf balls.

The cover compositions which may be used in making the golf balls of the present invention are set forth in detail but not limited to those in copending U.S. Ser. No. 07/776,803 filed Oct. 15, 1991, and Ser. No. 07/901,660 filed Jun. 19, 1992, both incorporated herein by reference. In short, the cover material is comprised of hard, high stiffness ionomer resins, preferably containing relatively high amounts of acid (i.e., greater than 16 weight percent acid, preferably from about 17 to about 25 weight percent acid, and more preferably from about 18.5 to about 21.5 weight percent) and at least partially neutralized with metal ions (such as sodium, zinc, potassium, calcium, magnesium and the like). The high acid resins are blended and melt processed to produce compositions exhibiting enhanced hardness and coefficient of restitution values when compared to low acid ionomers, or blends of low acid ionomer resins containing 16 weight percent acid or less.

The preferred cover compositions are made from specific blends of two or more high acid ionomers with other cover additives which do not exhibit the processing, playability, distance and/or durability limitations demonstrated by the prior art. However, as more particularly indicated below, the cover composition can also be comprised of one or more low acid ionomers so long as the molded covers exhibit a hardness of 65 or more on the Shore D scale.

Through the use of the softer cores and the hard cover, overall finished balls of the invention exhibit significantly lower spin rates than conventional balls of equal size and weight. Further, reduction in spin are also produced by increasing the thickness of the cover and by decreasing the weight of the softened core.

Further scope of the applicability of the present invention will become apparent from the detailed description given hereinafter. It should, however, be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the development of a golf ball having a low spin rate as a result of combining a relatively soft core and a hard cover. Such a lower spin rate after club impact contributes to straighter shots when the ball is mis-hit, greater efficiency in flight, and a lesser degree of energy loss on impact with the ground, adding increased roll or distance. In addition, by increasing the diameter of the overall ball of the present invention beyond the U.S.G.A. minimum of 1.680 inches, the spin rate is still further decreased by up to around 500 r.p.m. or more upon being hit with a No. 9 iron travelling at a speed of 105 feet per second (fps). In this embodiment of the invention, the ball, even though of larger diameter, uses substantially the same size

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core as a standard golf ball, the difference in size is provided by the additional thickness in the cover of the ball. This larger, low spin ball produces even greater control and flight efficiency than the standard size ball embodiment of the present invention.

Notwithstanding the overall size differences of the various embodiments of the present invention, the core of the present invention is relatively soft and of similar size. It has a Riehle compression of about 0.075 or more, preferably about 0.075 to about 0.115, and a relatively low PGA compression of about 40 to 85, preferably about 70-80.

The specially produced core compositions and resulting molded cores of the present invention are manufactured using relatively conventional techniques. In this regard, the core compositions of the invention may be based on polybutadiene, and mixtures of polybutadiene with other elastomers. It is preferred that the base elastomer have a relatively high molecular weight. The broad range for the molecular weight of suitable base elastomers is from about 50,000 to about 500,000. A more preferred range for the molecular weight of the base elastomer is from about 100,000 to about 500,000. As a base elastomer for the core composition, cis-polybutadiene is preferably employed, or a blend of cis-polybutadiene with other elastomers may also be utilized. Most preferably, cis-polybutadiene having a weight-average molecular weight of from about 100,000 to about 500,000 is employed. Along this line, it has been found that the high cis-polybutadiene manufactured and sold by Shell Chemical Co., Houston, Tex., under the tradename Cariflex BR-1220, and the polyisoprene available from Muehlstein, H & Co., Greenwich, Conn. under the designation "SKI 35" are particularly well suited.

The unsaturated carboxylic acid component of the core composition (a co-crosslinking agent) is the reaction product of the selected carboxylic acid or acids and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin, and the like. Preferably, the oxides of polyvalent metals such as zinc, magnesium and cadmium are used, and most preferably, the oxide is zinc oxide.

Exemplary of the unsaturated carboxylic acids which find utility in the present core compositions are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid, and the like, and mixtures thereof. Preferably, the acid component is either acrylic or methacrylic acid. Usually, from about 15 to about 25, and preferably from about 17 to about 21 parts by weight of the carboxylic acid salt, such as zinc diacrylate, is included in the core composition. The unsaturated carboxylic acids and metal salts thereof are generally soluble in the elastomeric base, or are readily dispersible.

The free radical initiator included in the core composition is any known polymerization initiator (a co-crosslinking agent) which decomposes during the cure cycle. The term "free radical initiator" as used herein refers to a chemical which, when added to a mixture of the elastomeric blend and a metal salt of an unsaturated, carboxylic acid, promotes crosslinking of the elastomers by the metal salt of the unsaturated carboxylic acid. The amount of the selected initiator present is dictated only by the requirements of catalytic activity as a polymerization initiator. Suitable initiators include peroxides, persulfates, azo compounds and hydrazides. Peroxides which are readily commercially available are conveniently used in the present invention, generally in amounts of from about 0.1 to about 10.0 and preferably in amounts of from about 0.3 to about 3.0 parts by weight per each 100 parts of elastomer.

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Exemplary of suitable peroxides for the purposes of the present invention are dicumyl peroxide, n-butyl 4,4'-bis (butylperoxy) valerate, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane, di-t-butyl peroxide and 2,5-di-(t-butylperoxy)-2,5 dimethyl hexane and the like, as well as mixtures thereof. It will be understood that the total amount of initiators used will vary depending on the specific end product desired and the particular initiators employed.

Examples of such commercially available peroxides are Luperco 230 or 231 XL sold by Atochem, Lucidol Division, Buffalo, N.Y., and Trigonox 17/40 or 29/40 sold by Akzo Chemie America, Chicago, Ill. In this regard Luperco 230 XL and Trigonox 17/40 are comprised of n-butyl 4,4-bis (butylperoxy) valerate; and, Luperco 231 XL and Trigonox 29/40 are comprised of 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane. The one hour half life of Luperco 231 XL is about 112° C., and the one hour half life of Trigonox 29/40 is about 129° C.

The core compositions of the present invention may additionally contain any other suitable and compatible modifying ingredients including, but not limited to, metal oxides, fatty acids, and diisocyanates and polypropylene powder resin. For example, Papi 94, a polymeric diisocyanate, commonly available from Dow Chemical Co., Midland, Mich., is an optional component in the rubber compositions. It can range from about 0 to 5 parts by weight per 100 parts by weight rubber (phr) component, and acts as a moisture scavenger. In addition, it has been found that the addition of a polypropylene powder resin results in a core which is too hard (i.e. exhibits low compression) and thus allows for a reduction in the amount of crosslinking agent utilized to soften the core to a normal or below normal compression.

Furthermore, because polypropylene powder resin can be added to core composition without an increase in weight of the molded core upon curing, the addition of the polypropylene powder allows for the addition of higher specific gravity fillers, such as mineral fillers. Since the crosslinking agents utilized in the polybutadiene core compositions are expensive and/or the higher specific gravity fillers are relatively inexpensive, the addition of the polypropylene powder resin substantially lowers the cost of the golf ball cores while maintaining, or lowering, weight and compression.

The polypropylene (C₃H₆) powder suitable for use in the present invention has a specific gravity of about 0.90 g/cm³, a melt flow rate of about 4 to about 12 and a particle size distribution of greater than 99% through a 20 mesh screen. Examples of such polypropylene powder resins include those sold by the Amoco Chemical Co., Chicago, Ill., under the designations "6400 P", "1700 P" and "7200 P". Generally, from 0 to about 25 parts by weight polypropylene powder per each 100 parts of elastomer are included in the present invention.

Various activators may also be included in the compositions of the present invention. For example, zinc oxide and/or magnesium oxide are activators for the polybutadiene. The activator can range from about 2 to about 30 parts by weight per 100 parts by weight of the rubbers (phr) component.

Moreover, filler-reinforcement agents may be added to the composition of the present invention. Since the specific gravity of polypropylene powder is very low, and when compounded, the polypropylene powder produces a lighter molded core, when polypropylene is incorporated in the core compositions, relatively large amounts of higher gravity fillers may be added so long as the specific core weight limitations are met. Additional benefits may be obtained by

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the incorporation of relatively large amounts of higher specific gravity, inexpensive mineral fillers such as calcium carbonate. Such fillers as are incorporated into the core compositions should be in finely divided form, as for example, in a size generally less than about 30 mesh and preferably less than about 100 mesh U.S. standard size. The amount of additional filler included in the core composition is primarily dictated by weight restrictions and preferably is included in amounts of from about 10 to about 100 parts by weight per 100 parts rubber.

The preferred fillers are relatively inexpensive and heavy and serve to lower the cost of the ball and to increase the weight of the ball to closely approach the U.S.G.A. weight limit of 1.620 ounces. However, if thicker cover compositions are to be applied to the core to produce larger than normal (i.e. greater than 1.680 inches in diameter) balls, use of such fillers and modifying agents will be limited in order to meet the U.S.G.A. maximum weight limitations of 1.620 ounces. Exemplary fillers include mineral fillers such as limestone, silica, micabarytes, calcium carbonate, or clays. Limestone is ground calcium/magnesium carbonate and is used because it is an inexpensive, heavy filler.

As indicated, ground flash filler may be incorporated and is preferably 20 mesh ground up center stock from the excess flash from compression molding. It lowers the cost and may increase the hardness of the ball.

Fatty acids or metallic salts of fatty acids may also be included in the compositions, functioning to improve moldability and processing. Generally, free fatty acids having from about 10 to about 40 carbon atoms, and preferably having from about 15 to about 20 carbon atoms, are used. Exemplary of suitable fatty acids are stearic acid and linoleic acids, as well as mixtures thereof. Exemplary of suitable metallic salts of fatty acids include zinc stearate. When included in the core compositions, the fatty acid component is present in amounts of from about 1 to about 25, preferably in amounts from about 2 to about 15 parts by weight based on 100 parts rubber (elastomer).

It is preferred that the core compositions include stearic acid as the fatty acid adjunct in an amount of from about 2 to about 5 parts by weight per 100 parts of rubber.

Diisocyanates may also be optionally included in the core compositions when utilized, the diisocyanates are included in amounts of from about 0.2 to about 5.0 parts by weight based on 100 parts rubber. Exemplary of suitable diisocyanates is 4,4'-diphenylmethane diisocyanate and other polyfunctional isocyanates known to the art.

Furthermore, the dialkyl tin difatty acids set forth in U.S. Pat. No. 4,844,471, the dispersing agents disclosed in U.S. Pat. No. 4,838,556, and the dithiocarbamates set forth in U.S. Pat. No. 4,852,884 may also be incorporated into the polybutadiene compositions of the present invention. The specific types and amounts of such additives are set forth in the above identified patents, which are incorporated herein by reference.

The core compositions of the invention are generally comprised of 100 parts by weight of a base elastomer (or rubber) selected from polybutadiene and mixtures of polybutadiene with other elastomers, 15 to 25 parts by weight of at least one metallic salt of an unsaturated carboxylic acid, and 1 to 10 parts by weight of a free radical initiator.

As indicated above, additional suitable and compatible modifying agents such as particulate polypropylene resin, fatty acids, and secondary additives such as Pecan shell flour, ground flash (i.e. grindings from previously manufactured cores of substantially identical construction), barium

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sulfate, zinc oxide, etc. may be added to the core compositions to adjust the weight of the ball as necessary in order to have the finished molded ball (core, cover and coatings) to closely approach the U.S.G.A. weight limit of 1.620 ounces.

In producing golf ball cores utilizing the present compositions, the ingredients may be intimately mixed using, for example, two roll mills or a Banbury mixer until the composition is uniform, usually over a period of from about 5 to about 20 minutes. The sequence of addition of components is not critical. A preferred blending sequence is as follows.

The elastomer, polypropylene powder resin (if desired), fillers, zinc salt, metal oxide, fatty acid, and the metallic dithiocarbamate (if desired), surfactant (if desired), and tin difatty acid (if desired), are blended for about 7 minutes in an internal mixer such as a Banbury mixer. As a result of shear during mixing, the temperature rises to about 200° F. The initiator and diisocyanate are then added and the mixing continued until the temperature reaches about 220° F. whereupon the batch is discharged onto a two roll mill, mixed for about one minute and sheeted out.

The sheet is rolled into a "pig" and then placed in a Barwell preformer and slugs are produced. The slugs are then subjected to compression molding at about 320° F. for about 14 minutes. After molding, the molded cores are cooled, the cooling effected at room temperature for about 4 hours or in cold-water for about one hour. The molded cores are subjected to a centerless grinding operation whereby a thin layer of the molded core is removed to produce a round core having a diameter of 1.540 to 1.545 inches. Alternatively, the cores are used in the as-molded state with no grinding needed to achieve roundness.

The mixing is desirably conducted in such a manner that the composition does not reach incipient polymerization temperatures during the blending of the various components.

Usually the curable component of the composition will be cured by heating the composition at elevated temperatures on the order of from about 275° F. to about 350° F., preferably and usually from about 290° F. to about 325° F., with molding of the composition effected simultaneously with the curing thereof. The composition can be formed into a core structure by any one of a variety of molding techniques, e.g. injection, compression, or transfer molding. When the composition is cured by heating, the time required for heating will normally be short, generally from about 10 to about 20 minutes, depending upon the particular curing agent used. Those of ordinary skill in the art relating to free radical curing agents for polymers are conversant with adjustments of cure times and temperatures required to effect optimum results with any specific free radical agent.

After molding, the core is removed from the mold and the surface thereof, preferably treated to facilitate adhesion thereof to the covering materials. Surface treatment can be effected by any of the several techniques known in the art, such as corona discharge, ozone treatment, sand blasting, and the like. Preferably, surface treatment is effected by grinding with an abrasive wheel.

The core is converted into a golf ball by providing at least one layer of covering material thereon, ranging in thickness from about 0.070 to about 0.130 inches and preferably from about 0.0675 to about 0.1275 inches.

The cover has a Shore D hardness of 65 or greater. Its composition includes a hard, high stiffness preferably high acid ionomer such as that sold by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or tradename

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"Iotek", or blends thereof. In addition to the Surlyn® and Escor® or Iotek ionomers, the cover may comprise any ionomer which either alone or in combination with other ionomers produces a molded cover having a Shore D hardness of at least 65. These include lithium ionomers or blends of ionomers with harder non-ionic polymers such as nylon, polyphenylene oxide and other compatible thermoplastics. As briefly mentioned above, examples of cover compositions which may be used are set forth in detail in copending U.S. Ser. No. 07/776,803 filed Oct. 15, 1991 and Ser. No. 07/901,660 filed Jun. 19, 1992, both incorporated herein by reference. Of course, the cover compositions are not limited in any way to those compositions set forth in said copending applications.

The high acid ionomers suitable for use in the present invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10–75%, preferably 30–70%) by the metal ions. Each of the high acid ionomer resins included in the cover compositions of the invention contains greater than about 16% by weight of a carboxylic acid, preferably from about 17% to about 25% by weight of a carboxylic acid, more preferably from about 18.5% to about 21.5% by weight of a carboxylic acid.

Although the cover composition preferably includes a high acid ionomeric resin and the scope of the patent embraces all known high acid ionomeric resins falling within the parameters set forth above, only a relatively limited number of these high acid ionomeric resins are currently available. In this regard, the high acid ionomeric resins available from E. I. DuPont de Nemours Company under the trademark "Surlyn®", and the high acid ionomer resins available from Exxon Corporation under the trademark "Escor®" or tradename "Iotek" are examples of available high acid ionomeric resins which may be utilized in the present invention.

The high acid ionomeric resins available from Exxon under the designation "Escor®" and or "Iotek", are somewhat similar to the high acid ionomeric resins available under the "Surlyn®" trademark. However, since the Escor®/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene acrylic acid) and the "Surlyn®" resins are zinc, sodium, magnesium, etc. salts of poly(ethylene methacrylic acid), distinct differences in properties exist.

Examples of the high acid methacrylic acid based ionomers found suitable for use in this invention include Surlyn® AD-8422 (sodium cation), Surlyn® 8162 (zinc cation), Surlyn® SEP-503-1 (zinc cation), and Surlyn® SEP-503-2 (magnesium cation). According to DuPont, all of these ionomers contain from about 18.5 to about 21.5% by weight methacrylic acid.

More particularly, Surlyn® AD-8422 is currently commercially available from DuPont in a number of different grades (i.e., AD-8422-2, AD-8422-3, AD-8422-5, etc.) based upon differences in melt index. According to DuPont, Surlyn® AD-8422 offers the following general properties when compared to Surlyn® 8920 the stiffest, hardest of all

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on the low acid grades (referred to as "hard" ionomers in U.S. Pat. No. 4,884,814):

	LOW ACID (15 wt % Acid)		HIGH ACID (>20 wt % Acid)	
	SURLYN® 8920	SURLYN® 8422-2	SURLYN® 8422-3	
IONOMER				
Cation	Na	Na	Na	
Melt Index	1.2	2.8	1.0	
Sodium, Wt %	2.3	1.9	2.4	
Base Resin MI	60	60	60	
MP ¹ , °C.	88	86	85	
FP, °C.	47	48.5	45	
COMPRESSION MOLDING²				
Tensile Break, psi	4350	4190	5330	
Yield, psi	2880	3670	3590	
Elongation, %	315	263	289	
Flex Mod, K psi	53.2	76.4	88.3	
Shore D hardness	66	67	68	

¹DSC second heat, 10° C./min heating rate.

²Samples compression molded at 150° C. annealed 24 hours at 60° C. 8422-2, -3 were homogenized at 190° C. before molding.

In comparing Surlyn® 8920 to Surlyn® 8422-2 and Surlyn® 8422-3, it is noted that the high acid Surlyn® 8422-2 and 8422-3 ionomers have a higher tensile yield, lower elongation, slightly higher Shore D hardness and much higher flexural modulus. Surlyn® 8920 contains 15 weight percent methacrylic acid and is 59% neutralized with sodium.

In addition, Surlyn® SEP-503-1 (zinc cation) and Surlyn® SEP-503-2 (magnesium cation) are high acid zinc and magnesium versions of the Surlyn® AD 8422 high acid ionomers. When compared to the Surlyn® AD 8422 high acid ionomers, the Surlyn SEP-503-1 and SEP-503-2 ionomers can be defined as follows:

Surlyn® Ionomer	Ion	Melt Index	Neutralization %
AD 8422-3	Na	1.0	45
SEP 503-1	Zn	0.8	38
SEP 503-2	Mg	1.8	43

Furthermore, Surlyn® 8162 is a zinc cation ionomer resin containing approximately 20% by weight (i.e. 18.5–21.5% weight) methacrylic acid copolymer that has been 30–70% neutralized. Surlyn® 8162 is currently commercially available from DuPont.

Examples of the high acid acrylic acid based ionomers suitable for use in the present invention include the Escor® or Iotek high acid ethylene acrylic acid ionomers produced by Exxon. In this regard, Escor® or Iotek 959 is a sodium ion neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to about 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are as follows:

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PROPERTY	ESCOR ® (IOTEK) 959	ESCOR ® (IOTEK) 960
Melt Index, g/10 min	2.0	1.8
Cation	Sodium	Zinc
Melting Point, °F.	172	174
Vicat Softening Point, °F.	130	131
Tensile @ Break, psi	4600	3500
Elongation @ Break, %	325	430
Hardness, Shore D	66	57
Flexural Modulus, psi	66,000	27,000

Furthermore, as a result of the development by the inventors of a number of new high acid ionomers neutralized to various extents by several different types of metal cations, such as by manganese, lithium, potassium, calcium and nickel cations, several new high acid ionomers and/or high acid ionomer blends besides sodium, zinc and magnesium high acid ionomers or ionomer blends are now available for golf ball cover production. It has been found that these new cation neutralized high acid ionomer blends produce cover compositions exhibiting enhanced hardness and resilience due to synergies which occur during processing. Consequently, the metal cation neutralized high acid ionomer resins recently produced can be blended to produce substantially harder covered golf balls having higher C.O.R.'s than those produced by the low acid ionomer covers presently commercially available.

More particularly, several new metal cation neutralized high acid ionomer resins have been produced by the inventors by neutralizing, to various extents, high acid copolymers of an alpha-olefin and an alpha, beta-unsaturated carboxylic acid with a wide variety of different metal cation salts. This discovery is the subject matter of U.S. application Ser. No. 901,680, incorporated herein by reference. It has been found that numerous new metal cation neutralized high acid ionomer resins can be obtained by reacting a high acid copolymer (i.e. a copolymer containing greater than 16% by weight acid, preferably from about 17 to about 25 weight percent acid, and more preferably about 20 weight percent acid), with a metal cation salt capable of ionizing or neutralizing the copolymer to the extent desired (i.e. from about 10% to 90%).

The base copolymer is made up of greater than 16% by weight of an alpha, beta-unsaturated carboxylic acid and an alpha-olefin. Optionally, a softening comonomer can be included in the copolymer. Generally, the alpha-olefin has from 2 to 10 carbon atoms and is preferably ethylene, and the unsaturated carboxylic acid is a carboxylic acid having from about 3 to 8 carbons. Examples of such acids include acrylic acid, methacrylic acid, ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, with acrylic acid being preferred.

The softening comonomer that can be optionally included in the invention may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms, vinyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

Consequently, examples of a number of copolymers suitable for use to produce the high acid ionomers included in the present invention include, but are not limited to, high

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acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight unsaturated carboxylic acid, from about 30 to about 83% by weight ethylene and from 0 to about 40% by weight of a softening comonomer. Preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remainder being ethylene.

Along these lines, examples of the preferred high acid base copolymers which fulfill the criteria set forth above, are a series of ethylene-acrylic copolymers which are commercially available from The Dow Chemical Company, Midland, Mich., under the "Primacor" designation. These high acid base copolymers exhibit the typical properties set forth below in Table 1.

TABLE 1

Typical Properties of Primacor Ethylene-Acrylic Acid Copolymers							
GRADE	PER- CENT ACID	DEN- SITY g/cc	MELT IN- DEX, °C	TEN- SILE YD. ST (psi)	FLEX- MODU- LUS (psi)	VI- CAT SOFT PT (°C.)	SHORE D HARD- NESS
ASTM		D-792	D-1238	D-638	D-790	D-1525	D-2240
5980	20.0	0.958	300.0	—	4800	43	50
5990	20.0	0.955	1300.0	650	2600	40	42
5990	20.0	0.955	1300.0	650	3200	40	42
5981	20.0	0.960	300.0	900	3200	46	48
5981	20.0	0.960	300.0	900	3200	46	48
5983	20.0	0.958	500.0	850	3100	44	45
5991	20.0	0.953	2600.0	635	2600	38	40

^aThe Melt Index values are obtained according to ASTM D-1238, at 190° C.

Due to the high molecular weight of the Primacor 5981 grade of the ethylene-acrylic acid copolymer, this copolymer is the more preferred grade utilized in the invention.

The metal cation salts utilized in the invention are those salts which provide the metal cations capable of neutralizing, to various extents, the carboxylic acid groups of the high acid copolymer. These include acetate, oxide or hydroxide salts of lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese.

Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. Suitable zinc ion sources are zinc acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide, magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

The new metal cation neutralized high acid ionomer resins are produced by reacting the high acid base copolymer with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a

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temperature from about 200° F. to about 500° F., preferably from about 250° F. to about 350° F. under high shear conditions at a pressure of from about 10 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the new metal cation neutralized high acid based ionomer resins is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in the high acid copolymer. The extent of neutralization is generally from about 10% to about 90%.

As indicated below in Table 2, more specifically in Example 1 in U.S. application Ser. No. 901,680, a number of new types of metal cation neutralized high acid ionomers can be obtained from the above indicated process. These include new high acid ionomer resins neutralized to various extents with manganese, lithium, potassium, calcium and nickel cations. In addition, when a high acid ethylene/acrylic acid copolymer is utilized as the base copolymer component of the invention and this component is subsequently neutralized to various extents with the metal cation salts producing acrylic acid based high acid ionomer resins neutralized with cations such as sodium, potassium, lithium, zinc, magnesium, manganese, calcium and nickel, several new cation neutralized acrylic acid based high acid ionomer resins are produced.

TABLE 2

Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness
1 (NaOH)	6.98	67.5	0.9	.804	71
2 (NaOH)	5.66	54.0	2.4	.808	73
3 (NaOH)	3.84	35.9	12.2	.812	69
4 (NaOH)	2.91	27.0	17.5	.812	(brittle)
5 (MnAc)	19.6	71.7	7.5	.809	73
6 (MnAc)	23.1	88.3	3.5	.814	77
7 (MnAc)	15.3	53.0	7.5	.810	72
8 (MnAc)	26.5	106	0.7	.813	(brittle)
9 (LiOH)	4.54	71.3	0.6	.810	74
10 (LiOH)	3.38	52.5	4.2	.818	72
11 (LiOH)	2.34	35.9	18.6	.815	72
12 (KOH)	5.30	36.0	19.3	Broke	70
13 (KOH)	8.26	57.9	7.18	.804	70
14 (KOH)	10.7	77.0	4.3	.801	67
15 (ZnAc)	17.9	71.5	0.2	.806	71
16 (ZnAc)	13.9	53.0	0.9	.797	69
17 (ZnAc)	9.91	36.1	3.4	.793	67
18 (MgAc)	17.4	70.7	2.8	.814	74
19 (MgAc)	20.6	87.1	1.5	.815	76
20 (MgAc)	13.8	53.8	4.1	.814	74
21 (CaAc)	13.2	69.2	1.1	.813	74
22 (CaAc)	7.12	34.9	10.1	.808	70

Controls:

50/50 Blend of Iotek 8000/7030 C.O.R. = .810/65 Shore D Hardness

DuPont High Acid Surlyn® 8422 (Na) C.O.R. = .811/70 Shore D Hardness

DuPont High Acid Surlyn® 8162 (Zn) C.O.R. = .807/65 Shore D Hardness

Exxon High Acid Iotek EX-960 (Zn) C.O.R. = .796/65 Shore D Hardness

23 (MgO) 2.91 53.5 2.5 .813

24 (MgO) 3.85 71.5 2.8 .808

25 (MgO) 4.76 89.3 1.1 .809

26 (MgO) 1.96 35.7 7.5 .815

Control for Formulations 23-26 is 50/50 Iotek 8000/7030,

C.O.R. = .814, Formulation 26 C.O.R. was normalized to that control accordingly

27 (NiAc) 13.04 61.1 0.2 .802 71

28 (NiAc) 10.71 48.9 0.5 .799 72

29 (NiAc) 8.26 36.7 1.8 .796 69

30 (NiAc) 5.66 24.4 7.5 .786 64

Control for Formulation Nos. 27-30 is 50/50 Iotek 8000/7030, C.O.R. = .807

When compared to low acid versions of similar cation neutralized ionomer resins, the new metal cation neutralized high acid ionomer resins exhibit enhanced hardness, modulus and resilience characteristics. These are properties that

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are particularly desirable in a number of thermoplastic fields, including the field golf ball manufacturing.

When utilized in golf ball cover construction, it has been found that the new acrylic acid based high acid ionomers extend the range of hardness beyond that previously obtainable while maintaining the beneficial properties (i.e. durability, click, feel, etc.) of the softer low acid ionomer covered balls, such as balls produced utilizing the low acid ionomers disclosed in U.S. Pat. Nos. 4,884,814 and 4,911,451, and the recently produced high acid blends disclosed in U.S. application Ser. No. 776,803.

Moreover, as a result of the development of a number of new acrylic acid based high acid ionomer resins neutralized to various extents by several different types of metal cations, such as manganese, lithium, potassium, calcium and nickel cations, several new ionomers or ionomer blends are now available for golf ball production. By using these high acid ionomer resins harder, stiffer golf balls having higher C.O.R.s, and thus longer distance, can be obtained.

As will be further noted in the Examples below, other ionomer resins may be used in the cover compositions, such as low acid ionomer resins, so long as the molded cover produces a Shore D hardness of 65 or more. Properties of some of these low acid ionomer resins are provided in the following table:

Typical Properties of Low Acid Escor® (Iotek) Ionomers							
Resin Properties	ASTM Method	Units	4000	4010	8000	8020	
Cation type			zinc	zinc	sodium	sodium	
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6	
Density	D-1505	kg/m ³	963	963	954	960	
35 Melting Point	D-3417	°C.	90	90	90	87.5	
Crystallization Point	D-3417	°C.	62	64	56	53	
Vicat Softening Point	D-1525	°C.	62	63	61	64	
% Weight Acrylic Acid			16	—	11	—	
40 % of Acid Groups Neutralized			30	—	40	—	
Plaque Properties	ASTM Method	Units	4000	4010	8000	8020	
45 (3 mm thick, compression molded)							
Tensile at Break	D-638	MPa	24	26	36	31.5	
50 Yield point	D-638	MPa	none	none	21	21	
Elongation at Break	D-638	%	395	420	350	410	
1% Secant modulus	D-638	MPa	160	160	300	350	
Shore D	D-2240	—	55	55	61	58	
55 Hardness D							
Resin Properties	ASTM Method	Units	8030	7010	7020	7030	
Cation type			sodium	zinc	zinc	zinc	
60 Melt Index	D-1238	g/10 min.	2.8	0.8	1.5	2.5	
Density	D-1505	kg/m ³	960	960	960	960	
Melting Point	D-3417	°C.	87.5	90	90	90	
Crystallization Point	D-3417	°C.	55	—	—	—	
Vicat Softening Point	D-1525	°C.	67	60	63	62.5	
% Weight			—	—	—	—	

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-continued

Typical Properties of Low Acid Escor® (Iotek) Ionomers						
Acrylic Acid % of Acid Groups	—	—	—	—	—	—
Cation Neutralized	—	—	—	—	—	—
Plaque Properties	ASTM Method	Units	8030	7010	7020	7030
(3 mm thick, compression molded)						
Tensile at Break	D-638	MPa	28	38	38	38
Yield Point	D-638	MPa	23	none	none	
Elongation at Break	D-638	%	395	500	420	395
1% Secant modulus	D-638	MPa	390	—	—	—
Shore Hardness D	D-2240	—	59	57	55	55

In addition to the above noted ionomers, compatible additive materials may also be added to produce the cover compositions of the present invention. These additive materials include dyes (for example, Ultramarine Blue sold by Whitaker, Clark, and Daniels of South Painsfield, N.J.), and pigments, i.e. white pigments such as titanium dioxide (for example Unitane 0-110) zinc oxide, and zinc sulfate, as well as fluorescent pigments. As indicated in U.S. Pat. No. 4,884,814, the amount of pigment and/or dye used in conjunction with the polymeric cover composition depends on the particular base ionomer mixture utilized and the particular pigment and/or dye utilized. The concentration of the pigment in the polymeric cover composition can be from about 1% to about 10% as based on the weight of the base ionomer mixture. A more preferred range is from about 1% to about 5% as based on the weight of the base ionomer mixture. The most preferred range is from about 1% to about 3% as based on the weight of the base ionomer mixture. The most preferred pigment for use in accordance with this invention is titanium dioxide.

Moreover, since there are various hues of white, i.e. blue white, yellow white, etc., trace amounts of blue pigment may be added to the cover stock composition to impart a blue white appearance thereto. However, if different hues of the color white are desired, different pigments can be added to the cover composition at the amounts necessary to produce the color desired.

In addition, it is within the purview of this invention to add to the cover compositions of this invention compatible materials which do not affect the basic novel characteristics of the composition of this invention. Among such materials are antioxidants (i.e. Santonox R), antistatic agents, stabilizers and processing aids. The cover compositions of the present invention may also contain softening agents, such as plasticizers, etc., and reinforcing materials such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers of the invention are not impaired.

Furthermore, optical brighteners, such as those disclosed in U.S. Pat. No. 4,679,795, may also be included in the cover composition of the invention. Examples of suitable optical brighteners which can be used in accordance with this invention are Uvitex OB as sold by the Ciba-Geigy Chemical Company, Ardsley, N.Y. Uvitex OB is thought to be 2,5-Bis(5-tert-butyl-2-benzoxazolyl)thiophene. Examples of other optical brighteners suitable for use in accordance with this invention are as follows: Leucopure EGM as sold by Sandoz, East Hanover, N.J. 07936. Leucopure EGM is

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thought to be 7-(2n-naphthol (1,2-d-triazol-2yl)-3phenyl-coumarin. Phorwhite K-20G2 is sold by Mobay Chemical Corporation, P.O. Box 385, Union Metro Park, Union, N.J. 07083, and is thought to be a pyrazoline derivative, Eastobrite OB-1 as sold by Eastman Chemical Products, Inc. Kingsport, Tenn., is thought to be 4,4-Bis(benzoxazolyl) stilbene. The above-mentioned Uvitex and Eastobrite OB-1 are preferred optical brighteners for use in accordance with this invention.

Moreover, since many optical brighteners are colored, the percentage of optical brighteners utilized must not be excessive in order to prevent the optical brightener from functioning as a pigment or dye in its own right.

The percentage of optical brighteners which can be used in accordance with this invention is from about 0.01% to about 0.5% as based on the weight of the polymer used as a cover stock. A more preferred range is from about 0.05% to about 0.25% with the most preferred range from about 0.10% to about 0.020% depending on the optical properties of the particular optical brightener used and the polymeric environment in which it is a part.

Generally, the additives are admixed with a ionomer to be used in the cover composition to provide a masterbatch (M. B.) of desired concentration and an amount of the masterbatch sufficient to provide the desired amounts of additive is then admixed with the copolymer blends.

The above cover compositions, when processed according to the parameters set forth below and combined with soft cores at thicknesses defined herein to produce covers having a Shore D hardness of 65, provide golf balls with reduced spin ratio. It is noted, however, that the high acid ionomer resins provide for more significant reduction in spin rate than that observed for the low acid ionomer resins.

The cover compositions and molded balls of the present invention may be produced according to conventional melt blending procedures. In this regard, the ionomeric resins are blended along with the masterbatch containing the desired additives in a Banbury type mixer, two-roll mill, or extruded prior to molding. The blended composition is then formed into slabs or pellets, etc. and maintained in such a state until molding is desired. Alternatively a simple dry blend of the pelletized or granulated resins and color masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process.

Moreover, golf balls of the present invention can be produced by molding processes currently well known in the golf ball art. Specifically, the golf balls can be produced by injection molding or compression molding the novel cover compositions about the soft polybutadiene cores to produce a golf ball having a diameter of about 1.680 inches or greater and weighing about 1.620 ounces. In an additional embodiment of the invention, larger molds are utilized to produce the thicker covered oversized golf balls.

As indicated, the golf balls of the present invention can be produced by forming covers consisting of the compositions of the invention around the softer polybutadiene cores by conventional molding processes. For example, in compression molding, the cover composition is formed via injection at about 380° F. to about 450° F. into smooth surfaced hemispherical shells which are then positioned around the core in a dimpled golf ball mold and subjected to compression molding at 200°-300° F. for 2-10 minutes, followed by cooling at 50°-70° F. for 2-10 minutes, to fuse the shells together to form an unitary ball. In addition, the golf balls may be produced by injection molding, wherein the cover composition is injected directly around the core placed in the

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center of a golf ball mold for a period of time at a mold temperature of from 50° F. to about 100° F. After molding the golf balls produced may undergo various further finishing steps such as buffing, painting, and marking as disclosed in U.S. Pat. No. 4,911,451.

The present invention is further illustrated by the following examples in which the parts of the specific ingredients are by weight (pbw). It is to be understood that the present invention is not limited to the examples, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

EXAMPLE 1

Using the ingredients tabled below, golf ball cores having a finished diameter of about 1.540 to about 1.545 inches were produced by compression molding and subsequent removal of a surface layer by grinding. Each core was formulated using 100 parts elastomer (rubber). In the formulations, the amounts of remaining ingredients are expressed in parts by weight, and the weight, degrees of coefficient of restitution and compression (both Riehle and PGA) achieved are set forth below. The data for these examples are the averages for twelve cores which were produced for each example. The properties of the molded cores produced from each formulation were measured according to the following parameters:

Riehle compression is a measurement of the deformation of a golf ball in thousandths of inches under a fixed static load of 200 pounds (a Riehle compression of 47 corresponds to a deflection under load of 0.47 inches).

PGA compression is determined by a force applied to a spring (i.e. 80 PGA=80 Riehle; 90 PGA=70 Riehle; and 100 PGA=60 Riehle) and manufactured by Atti Engineering, Union City, N.J.

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air cannon at a velocity of 125 feet per second against a steel plate which is positioned 12 feet from the muzzle of the cannon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give the coefficient of restitution.

The following core formulations were prepared according to the methods set forth above:

CORE COMPOSITIONS				
	A	B	C	D
<u>Ingredients</u>				
BR-1220 ¹	100	100	100	100
Zinc Diacrylate	18	20	37	26
Ground Flash	17	20	20	17
Zinc Oxide	6	6	6	6
Limestone	7	25	15	—
Zinc Stearate	15	20	20	15
6400 Polypropylene ²	10	—	—	10
Trigonox 17/40 ³	1.5	1.5	1.5	1.5
Papi 94 ⁴	0.5	0.5	0.5	0.5
<u>Molded Core Properties</u>				
Core Diameter (in.)	1.541	1.542	1.543	1.542
Weight (grams)	33.7	36.5	36.8	33.8
Compression (Riehle/PGA)	87/73	83/77	64/96	74/86
C.O.R. (e)	.773	.782	.802	.787

¹BR-1220 is a polybutadiene manufactured and sold by Shell Chemical Co., Houston, Tex.

²6400 P. is a powdered polypropylene available from Amco Chemical Co., Chicago, Ill.

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³Trig 17/40 is a peroxide manufactured and sold by Akzo Chemie, Chicago, Ill. (one hour half life is at 129° C.).

⁴Papi 94 is a polymeric diisocyanate available from Dow Chemical Co., Midland, Mich.

As noted by the above indicated data, core formulations A and B produce softer cores. Formulation A is appropriate for a molded ball having an overall diameter of about 1.720 inches (i.e., 1.117"). It has less filler, hence a lower specific gravity, than formulation B which is appropriate for a smaller ball, one having a diameter of about 1.680 inches. Formulations C and D are for conventional harder cores. Formulation C is slightly heavier and used for a ball having a diameter of about 1.680 inches. Formulation D is used for producing a ball having a diameter of about 1.720 inches (1.717").

EXAMPLE 2

Cover compositions were produced by blending the following constituents:

Ingredients	COVER COMPOSITIONS		
	Cover 1	Cover 2	Cover 3
Iotek 8000	45.2	—	22.6
Iotek 7030	45.2	—	22.6
Iotek 959	—	45.2	—
Iotek 960	—	45.2	—
Iotek 7520 ¹	—	—	45.2
White MB ²	9.6	9.6	9.6

¹Iotek 7520 is a relatively soft, low acid, ionomer resin produced by Exxon.

²MB = 74.9 wt-% Iotek 7030, 23.8 wt-% TiO₂, 0.01 wt-% Unitex OB, 0.002 wt-% ultra marine blue and 300 ppm Santonox R.

¹Iotek 7520 is a relatively soft, low acid, ionomer resin produced by Exxon.

²MB=74.9 wt-% Iotek 7030, 23.8 wt-% TiO₂, 0.02 wt-% Unitex OB, 0.002 wt-% ultra marine blue and 300 ppm Santonox R.

Of the three cover formulations provided above, formulation 2 is the hardest. It is comprised of two hard, high acid ionomer resins. Iotek 959 has an acid content of about 19% to 21% and Iotek 960 also has an acid content of about 19 to 21%.

Formulation 3 provides the softest of the three cover formulations and is substantially similar to the formulation used in the TOP-FLITE TOUR EDITION 90 golf ball. Formulation 3 is Comprised of Iotek 8000 and Iotek 7030, both hard, low acid ionomers, and Iotek 7520, a soft, low-acid ionomer, in the amounts set forth above.

Formulation 1 provides intermediate hardness, and is essentially the same formulation used in the TOP FLITE XL II ball (see U.S. Pat. No. 4,911,481).

EXAMPLE 3

The cover formulations set forth in Example 2 were injection molded at about 400° F. around cores of formulations A–D in Example 1 in a manner to permit uniform injection of the selected cover composition over each core. Each of the cores had an identical finished diameter of about 1.541–1.543 inches to produce golf balls of approximately 1.720 (1.717) inches (cores A and D) or about 1.680 inches (cores B and C) in diameter. The cover thickness varied between about 0.069 and about 0.088 inches. All materials were molded under essentially identical conditions. The properties of Riehle compression, PGA compression, coefficient of restitution (C.O.R.), barrel durability (100 blows), cover hardness and spin rate were determined. The results are set forth in Table 3 below.

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The data for each example represents the average data for one dozen balls produced according to the desired manner. The properties were measured according to the following parameters:

Coefficient of restitution (C.O.R.) was measured by firing the resulting golf ball in an air cannon at a velocity of 125 feet per second against a steel plate which is positioned 12 feet from the muzzle of the cannon. The rebound velocity was then measured. The rebound velocity was divided by the forward velocity to give the coefficient of restitution.

Shore hardness was measured in accordance with ASTM Test D-2240.

The barrel test or barrel durability test involves firing golf balls at 135 ft./sec. (at 72° F.), into a 5-sided container, the walls of which are steel plates that have grooves milled into them to simulate a golf club face. The balls are subjected to 100 to 300 blows and are inspected at regular intervals for breakage (i.e. any signs of cover cracking or delamination). NB=no breakage.

The spin rate of the golf ball was measured by striking the resulting golf balls with a 9-iron wherein the club-head speed is about 105 feet per second and the ball is launched at an angle of 26 to 34 degrees with an initial velocity of about 110–115 feet per second. The spin rate was measured by observing the rotation of the ball in flight using stop action Strobe photography.

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formulation tested (formulation 2) provides for golf balls having the lowest spin rate.

Further reduction in spin rate is observed through the use of a soft core (core A and B) with the hardest cover (cover formulation 2), with the largest reduction in spin rate observed through the use of the softest core (core A) with the hardest cover (cover formulation 2).

It should be further noted that increased diameter provides for lower spin rates. In comparing balls A,1–3 with corresponding balls B,1–3, the balls having the larger diameter (A,1–3) are lower in spin than balls B,1–3, respectively. The C.O.R. and compression are controlled mainly by the core formulation, with a hard fast core giving a harder, faster ball.

As ball diameter increases upon increasing the cover thickness (core diameter remains the same), the thicker cover (0.0888 versus 0.0690 inches) provides for significant C.O.R. pick-up from center to ball. Further, the increased cover thickness play a role in added spin reduction observed for the larger balls.

With attention still focused on the tabulated results, the combination of a soft core with a hard cover gives the lowest spin. In comparing ball A,2 to ball D,2 (both at 1.72 inches in diameter) it is seen that the softer core A contributes to lower spin rates. Combination A,2 (softer core, hardest cover) provides the lowest spin rate for the entire test. These same trends hold for the smaller balls, i.e. ball B,2 is lower in spin than ball C,2. While ball B,2 is the lowest spin among the 1.68 inch balls, its spin rate is not as low as ball A,2 which

TABLE 3

Bell/Type (Core/Cover)	Ball Size	Riehle Comp.	PGA Comp.	C.O.R.	Barrel Durability (100 blows)	Cover Hardness Shore C/D	Spin Rate #9 Iron (105 fps)
A,1	1.72	62	98	.814	NB	96/65	7019
A,2	1.72	59	101	.827	NB	97/68	6544
A,3	1.72	65	95	.795	NB	87/56	8409
B,1	1.68	61	99	.793	NB	95/65	7541
B,2	1.68	57	103	.803	NB	97/68	6755
B,3	1.68	62	98	.775	NB	87/56	8764
C,1	1.68	49	111	.816	NB	95/65	7643
C,2	1.68	47	113	.822	NB	97/68	6933
C,3	1.68	50	110	.805	NB	87/56	9231
D,1	1.72	57	103	.820	NB	95/65	7285
D,2	1.72	55	105	.830	NB	97/68	6816
D,3	1.72	58	102	.802	NB	87/56	8578

For comparison purposes, the same results are provided for known preexisting golf balls:

has a larger diameter. This is believed to be attributed to the differences in cover thickness.

Bell/Type (Core/Cover)	Ball Size	Riehle Comp.	PGA Comp.	C.O.R.	Barrel Durability (100 blows)	Cover Hardness Shore C/D	Spin Rate #9 Iron (105 fps)
Titleist Tour 100	1.68	73	87	.792	NB	83/51	9676
Tour Edition 100	1.68	58	102	.802	NB	85/53	9961
Tour Edition 90	1.68	56	104	.802	NB	87/56	9621
Top-Flite XL II	1.68	51	109	.810	NB	95/65	7163

Molded ball spin test results show that notwithstanding differences in ball size, the combination of a soft core (cores A and B) with a hard cover (cover formulations 1 and 2) minimizes spin rate. Even in the instance where harder cores are used (cores C and D) the golf ball with the hardest cover

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon a reading and understanding of the preceding detailed description. It is intended that the invention be construed as including all such alterations and

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modifications insofar as they come within the scope of the appended claims or the equivalents thereof.

Having thus described the invention, it is claimed:

1. A golf ball, comprising:

a core comprising a diene polymer having a Riehle 5
compression of at least 0.075; and

a cover having a Shore D hardness of at least 65, wherein
the cover is comprised of at least one high acid ionomer
resin comprising a copolymer of greater than 16% by
weight of an alpha, beta-unsaturated carboxylic acid, 10
and an alpha olefin of which about 10 to about 90% of
the carboxyl groups of the copolymer are neutralized
with a metal cation.

2. A golf ball comprising:

a core comprising a diene polymer having a Riehle 15
compression of at least 0.075; and

a cover comprising an ionomer resin and having a Shore
D hardness of at least 65 and a thickness of 0.10 to 0.13
inches.

3. A golf ball, as set forth in claim 2, wherein the golf ball
has a diameter of 1.700–1.800 inches.

4. A golf ball, as set forth in claim 2, wherein the golf ball
has a diameter of 1.710–1.730 inches.

5. A golf ball, as set forth in claim 2, wherein the golf ball
has a diameter of 1.717–1.720 inches.

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6. A golf ball comprising:

a core comprising a diene polymer having a Riehle
compression of at least 0.075; and

a cover comprising an ionomer resin and having a Shore
D hardness of at least 65 and a thickness of 0.09 to 0.13
inches.

7. A golf ball, as set forth in claim 6, wherein the golf ball
has a diameter of 1.700–1.800 inches.

8. A golf ball, as set forth in claim 6, wherein the golf ball
has a diameter of 1.710–1.730 inches.

9. A golf ball, as set forth in claim 6, wherein the golf ball
has a diameter of 1.717–1.720 inches.

10. A golf ball comprising:

a core comprising a diene polymer having a Riehle
compression of at least 0.075; and

a cover comprising an ionomer resin and having a Shore
D hardness of at least 65 and a thickness of 0.08 to 0.13
inches.

11. A golf ball, as set forth in claim 10, wherein the golf
ball has a diameter of 1.710–1.800 inches.

12. A golf ball, as set forth in claim 10, wherein the golf
ball has a diameter of 1.710–1.730 inches.

13. A golf ball, as set forth in claim 10, wherein the golf
ball has a diameter of 1.717–1.720 inches.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,820,489
DATED : October 13, 1998
INVENTOR(S) : Michael J. Sullivan and R. Dennis Nesbitt

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 20, line 51, delete "4,911,481" and insert therefor --4,911,451--.

Column 19, line 30, "0.47" should read --0.047--.

Signed and Sealed this

Twenty-sixth Day of September, 2000

Attest:



Q. TODD DICKINSON

Attesting Officer

Director of Patents and Trademarks

**DECLARATION OF THOMAS L. HALKOWSKI
IN SUPPORT OF CALLAWAY GOLF'S
MOTION *IN LIMINE* TO EXCLUDE
ACUSHNET'S "TEST BALLS" AND RELATED
TESTIMONY**

EXHIBIT 3



US005932038A

United States Patent [19][11] **Patent Number:** **5,932,038****Bach et al.**[45] **Date of Patent:** **Aug. 3, 1999**[54] **METHOD OF FABRICATING A STRAW
PANEL, BOARD, OR BEAM**[75] Inventors: **Lars Bach; Kenneth W. Domier;
Raymond Holowach**, all of Edmonton,
Canada[73] Assignee: **Alberta Research Council**, Edmonton,
Canada

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[21] Appl. No.: **09/119,041**[22] Filed: **Jul. 20, 1998**[30] **Foreign Application Priority Data**

Jul. 24, 1997	[CA]	Canada	2211472
Apr. 15, 1998	[CA]	Canada	2234889

[51] **Int. Cl.⁶** **B32B 5/12; B32B 31/20**[52] **U.S. Cl.** **156/62.2; 156/259; 156/296;
156/433; 264/113; 264/437**[58] **Field of Search** **156/62.2, 296,
156/433, 259, 271; 264/108, 109, 113,
437; 198/382, 533; 425/110**[56] **References Cited****U.S. PATENT DOCUMENTS**

4,505,777 3/1985 Richter .

Primary Examiner—Sam Chuan Yao*Attorney, Agent, or Firm*—Neil Teitelbaum & Associates[57] **ABSTRACT**

A structural panel, board, or beam and method of making same, with straw that is oriented is provided. The straw is preferably oriented such that strands are parallel oriented in one or more directions. The straw strands are chopped, split, and a binder such as MDI is added.

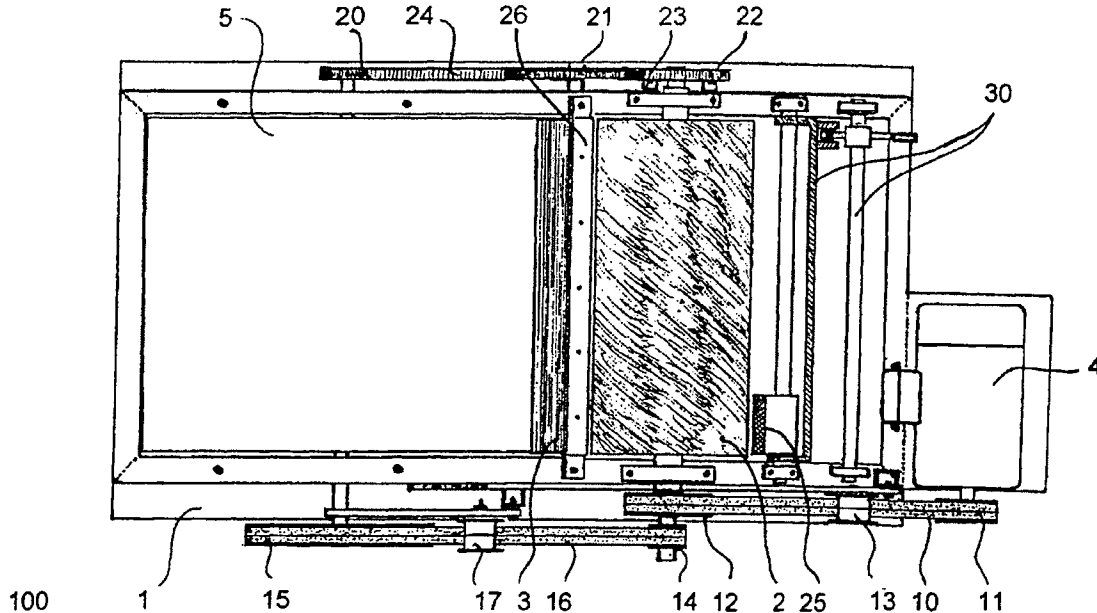
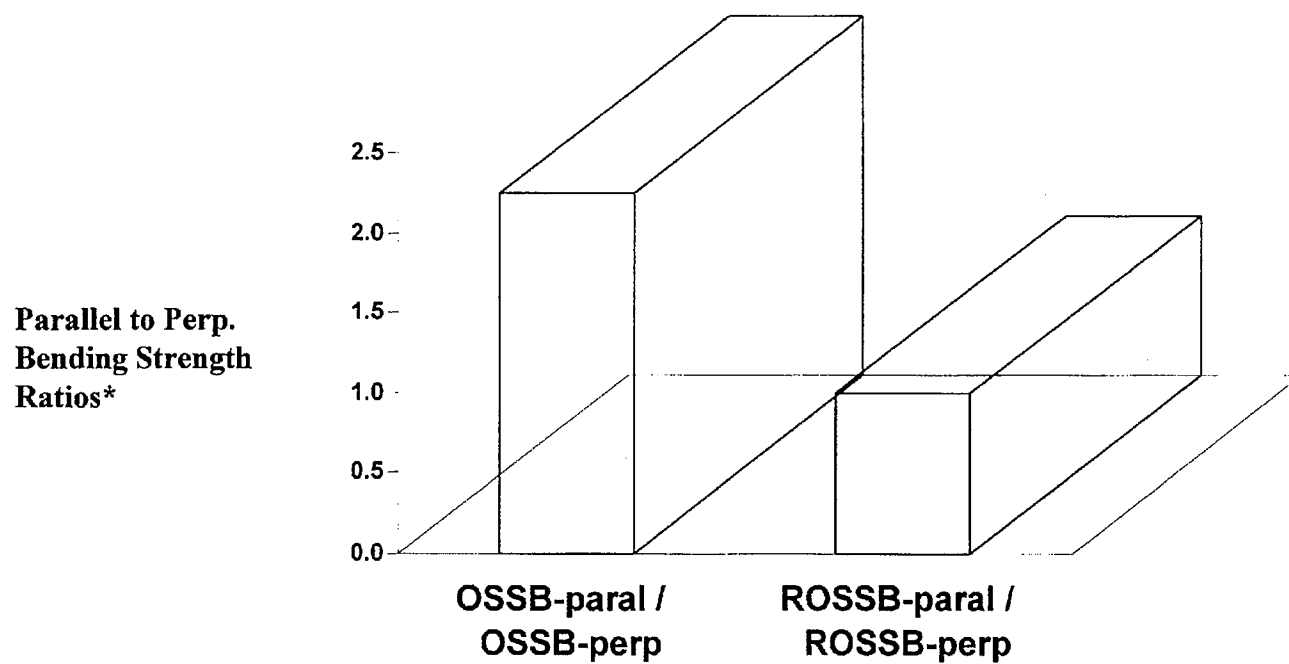
15 Claims, 14 Drawing Sheets

Fig. 1



*Modulus of Rupture (MOR) in the parallel direction divided with MOR in the perpendicular direction of the same panel

Fig. 2

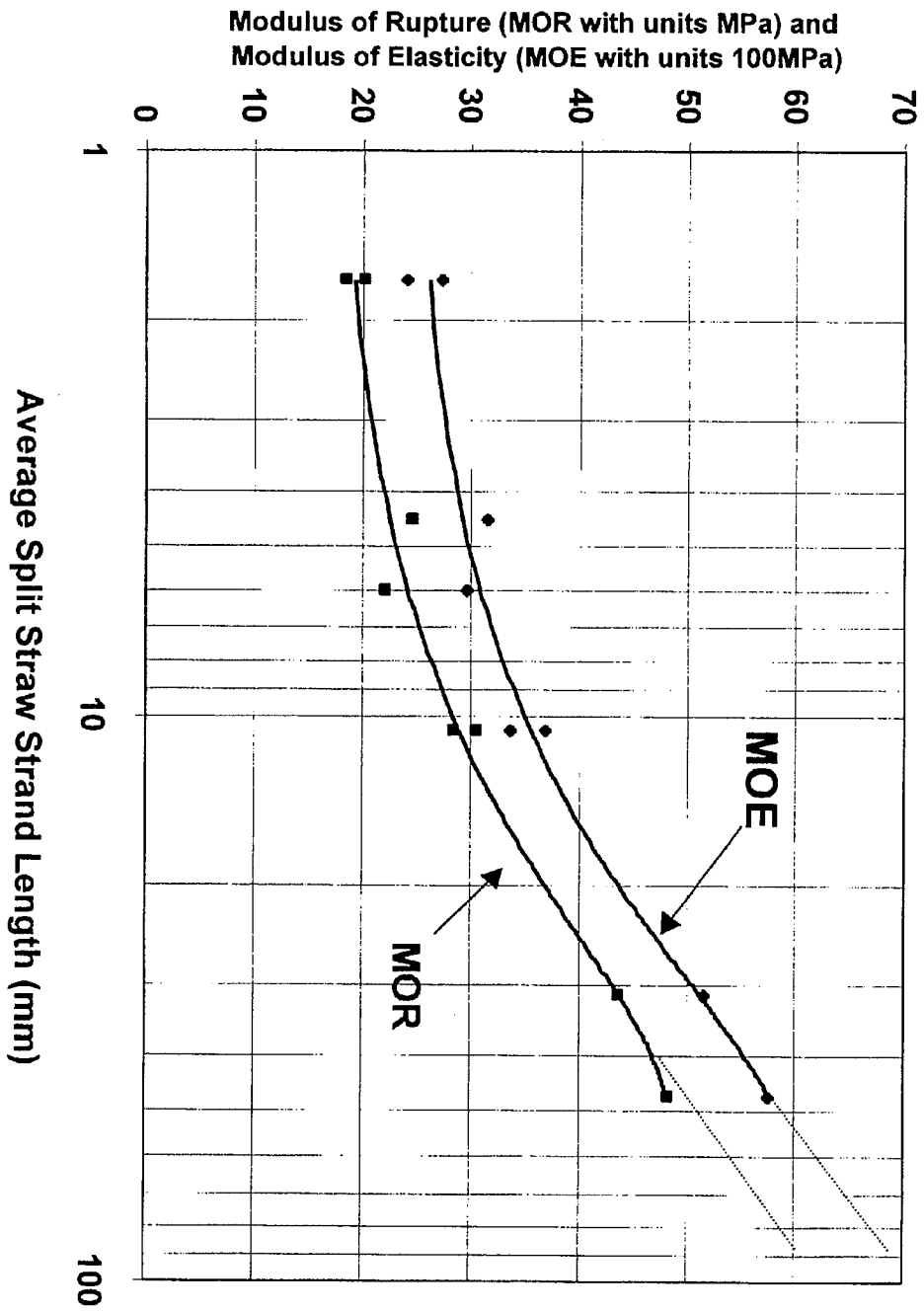


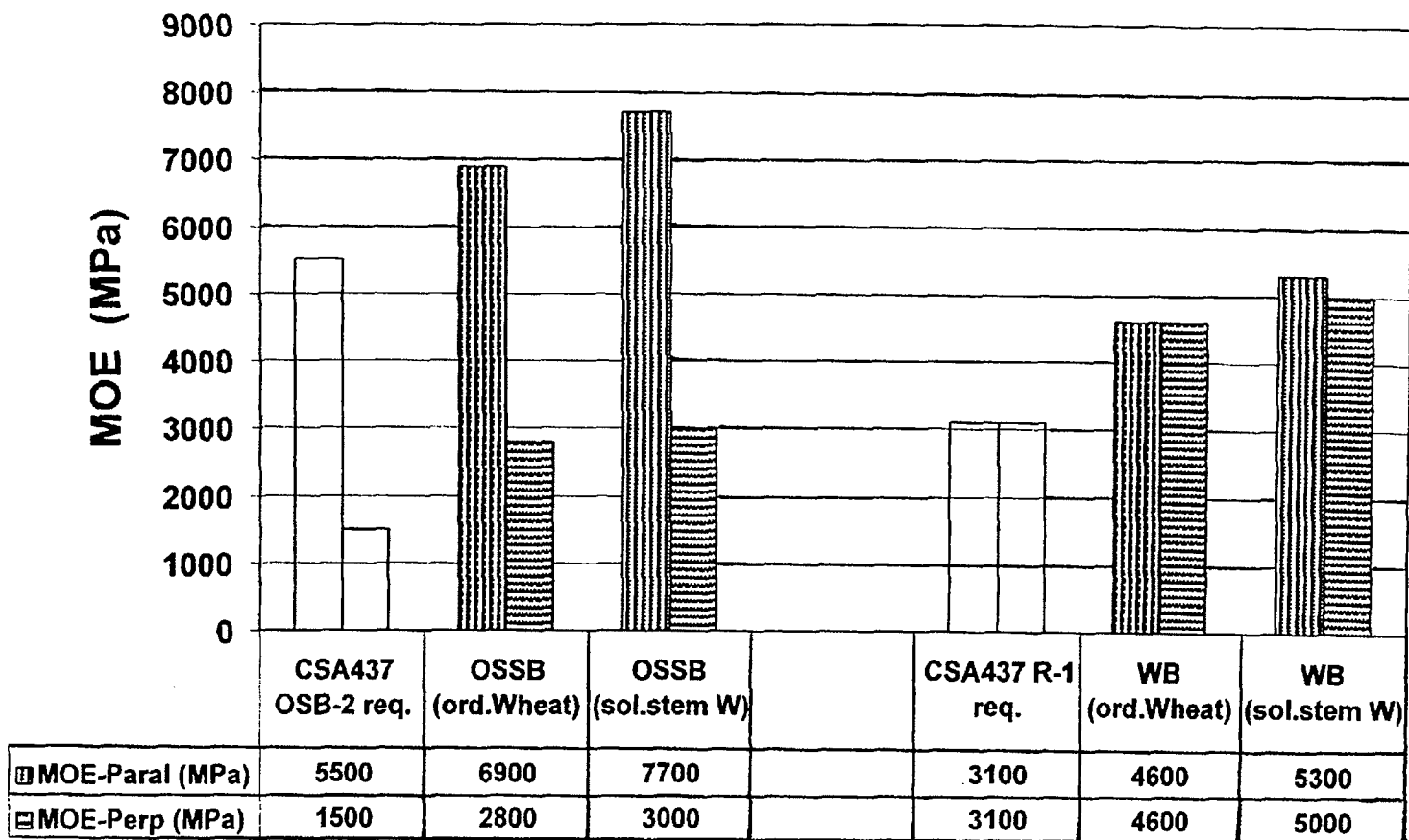
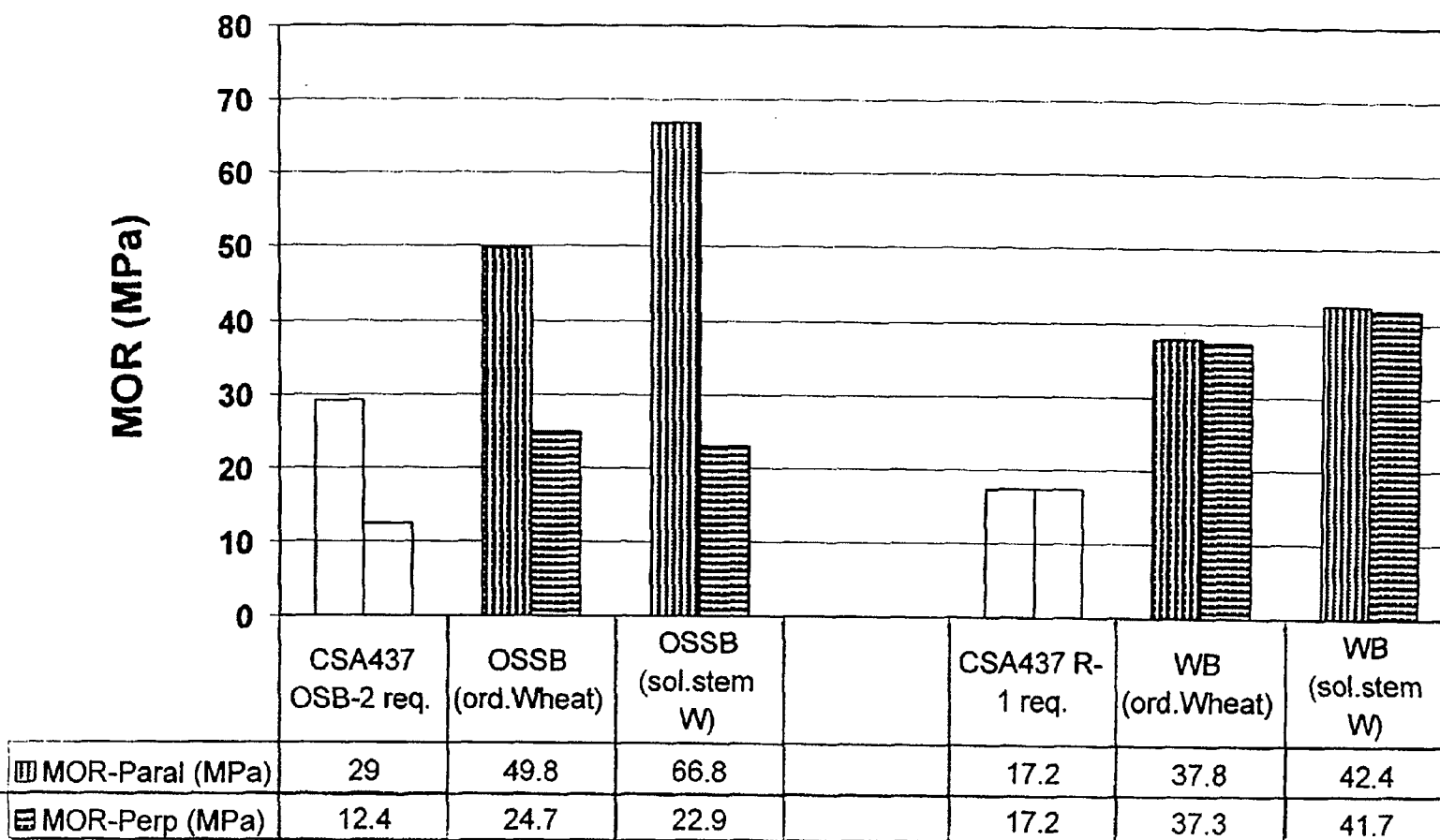
Fig. 3

Fig. 4

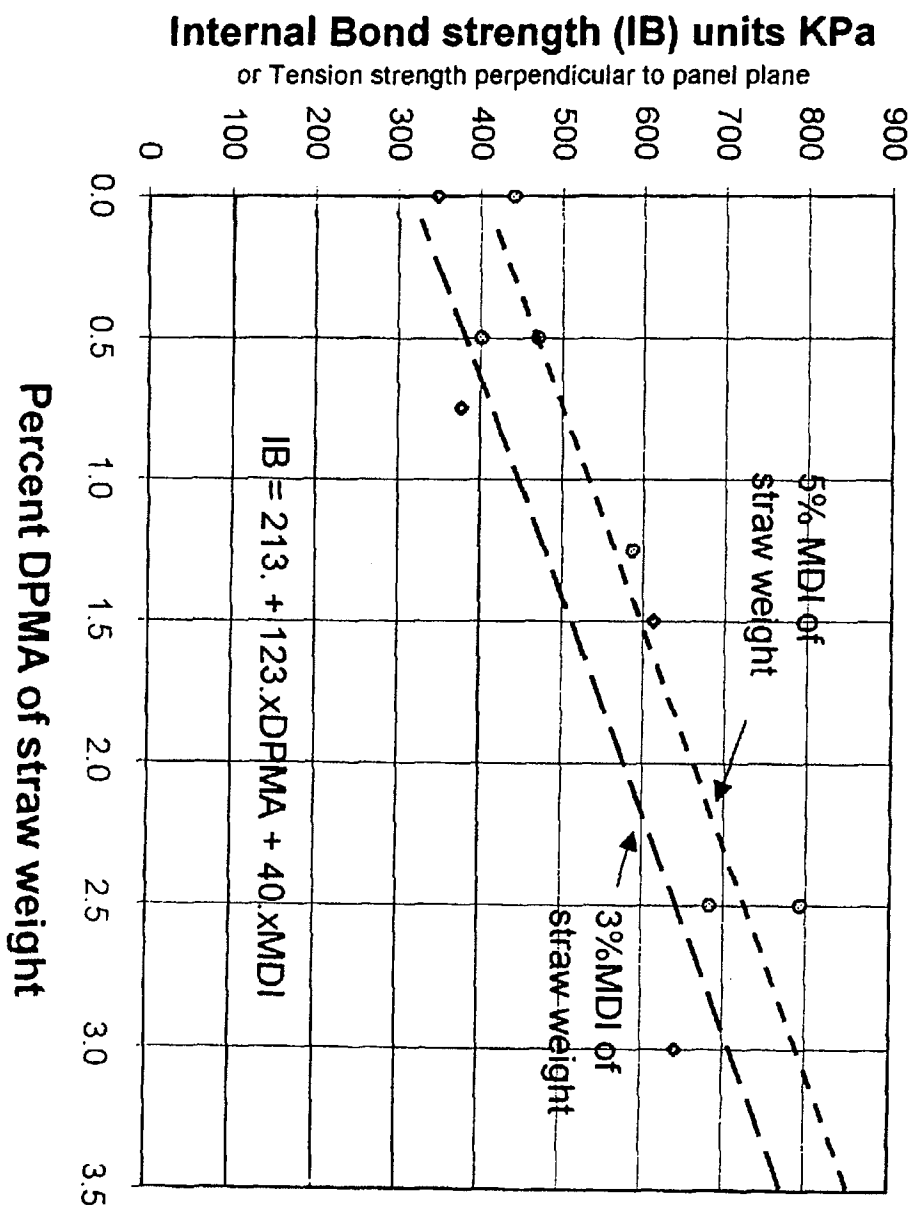


Fig. 5

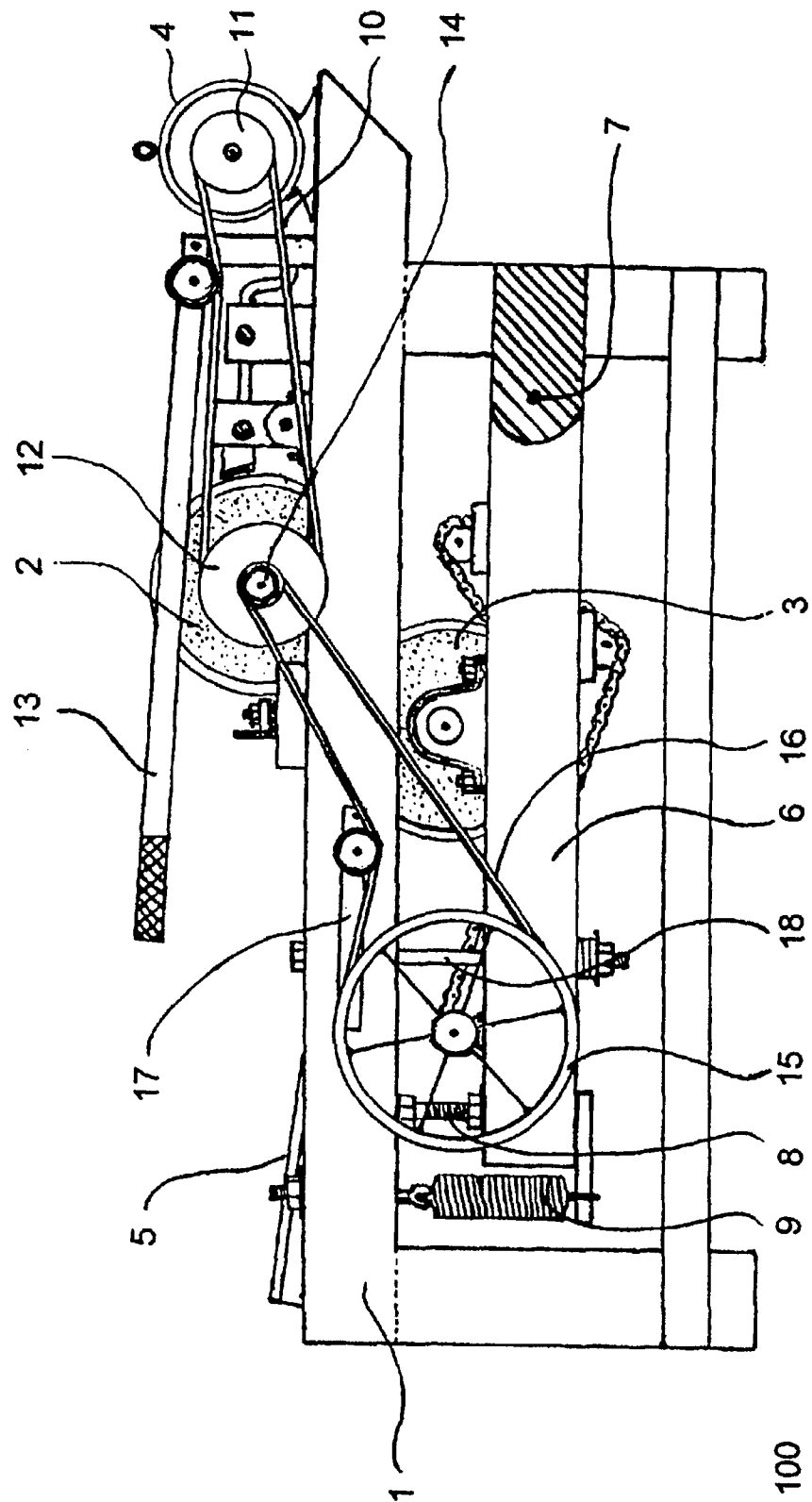
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Fig. 6



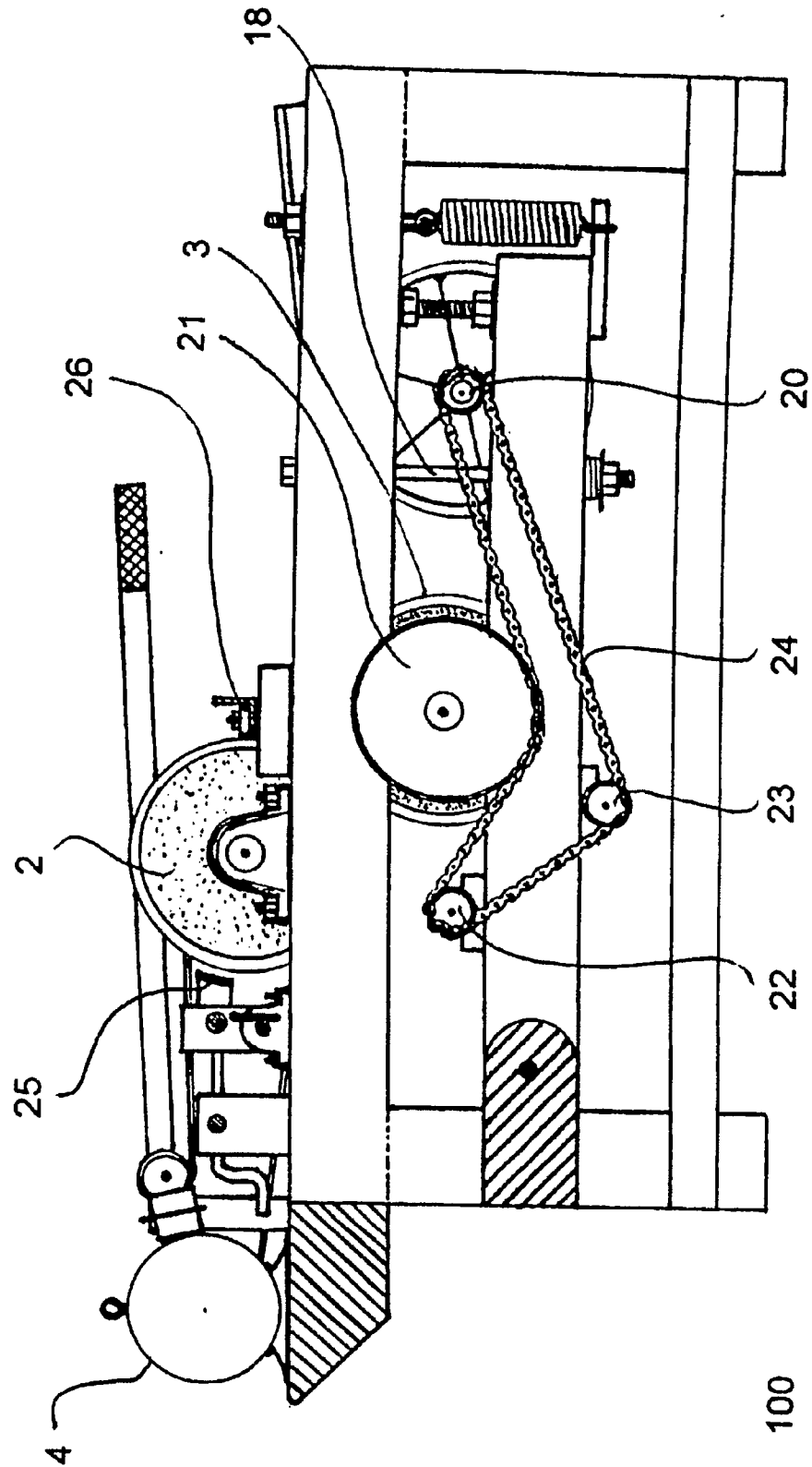
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Fig. 7



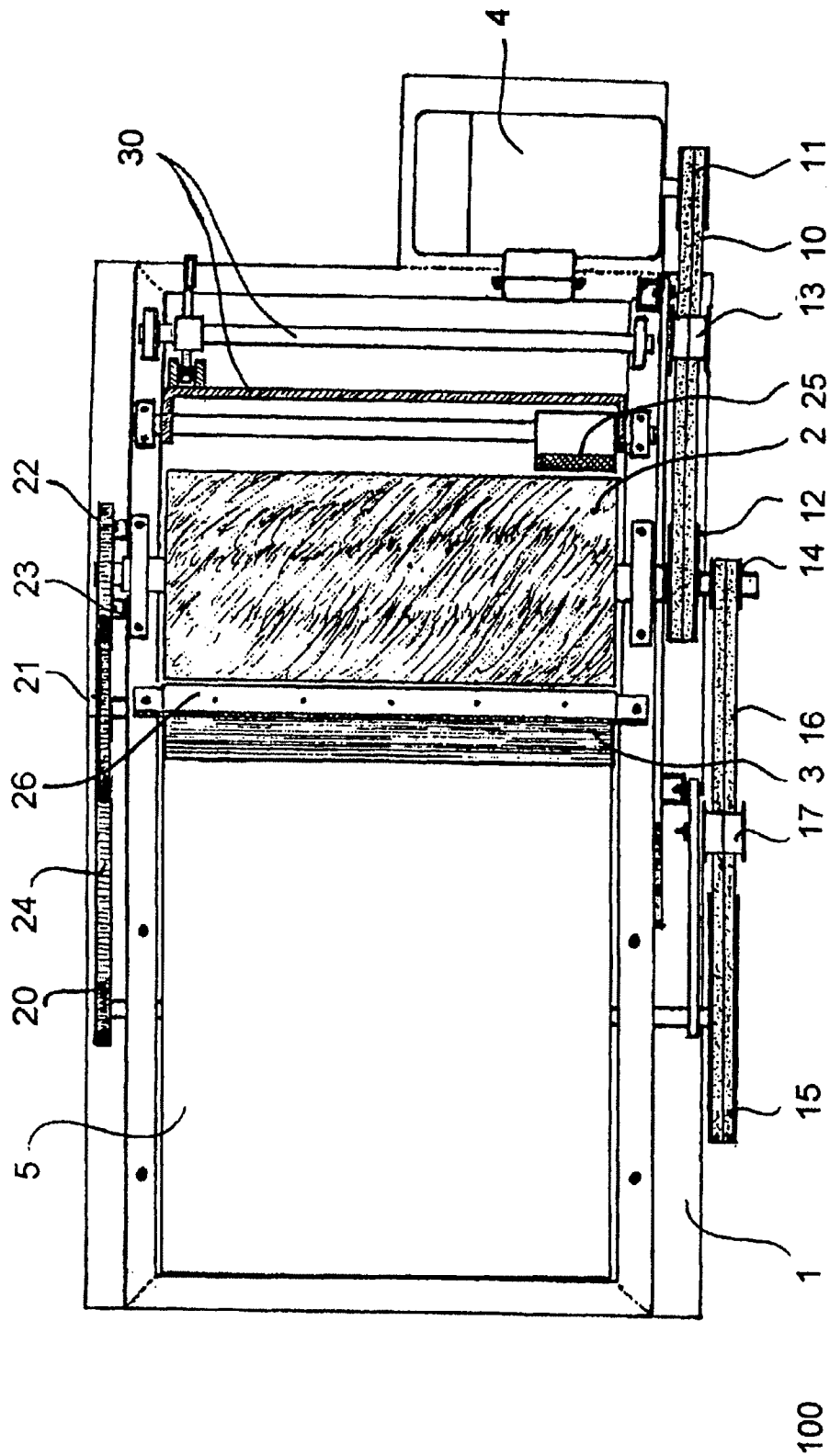
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Fig. 8



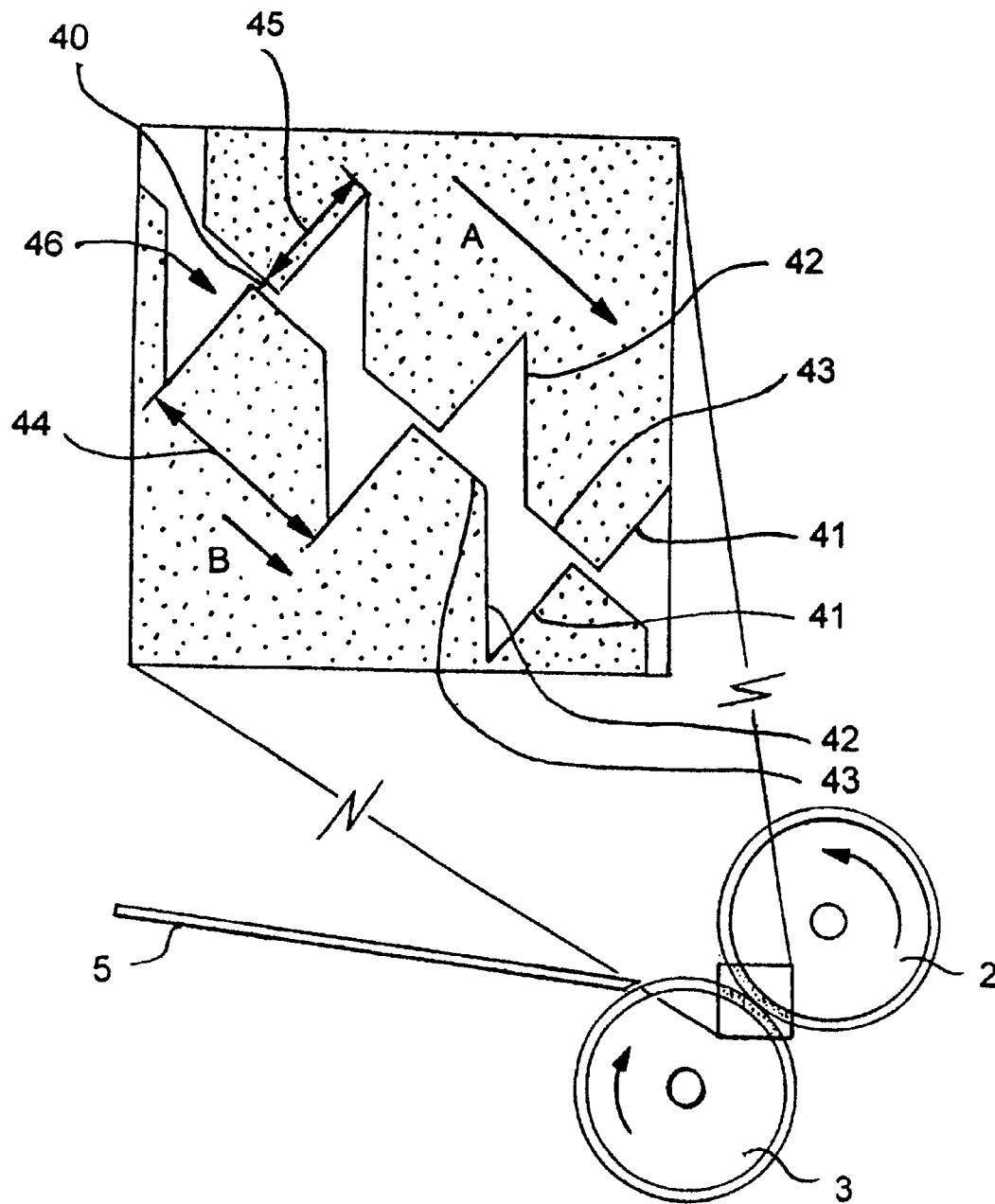
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Fig. 9

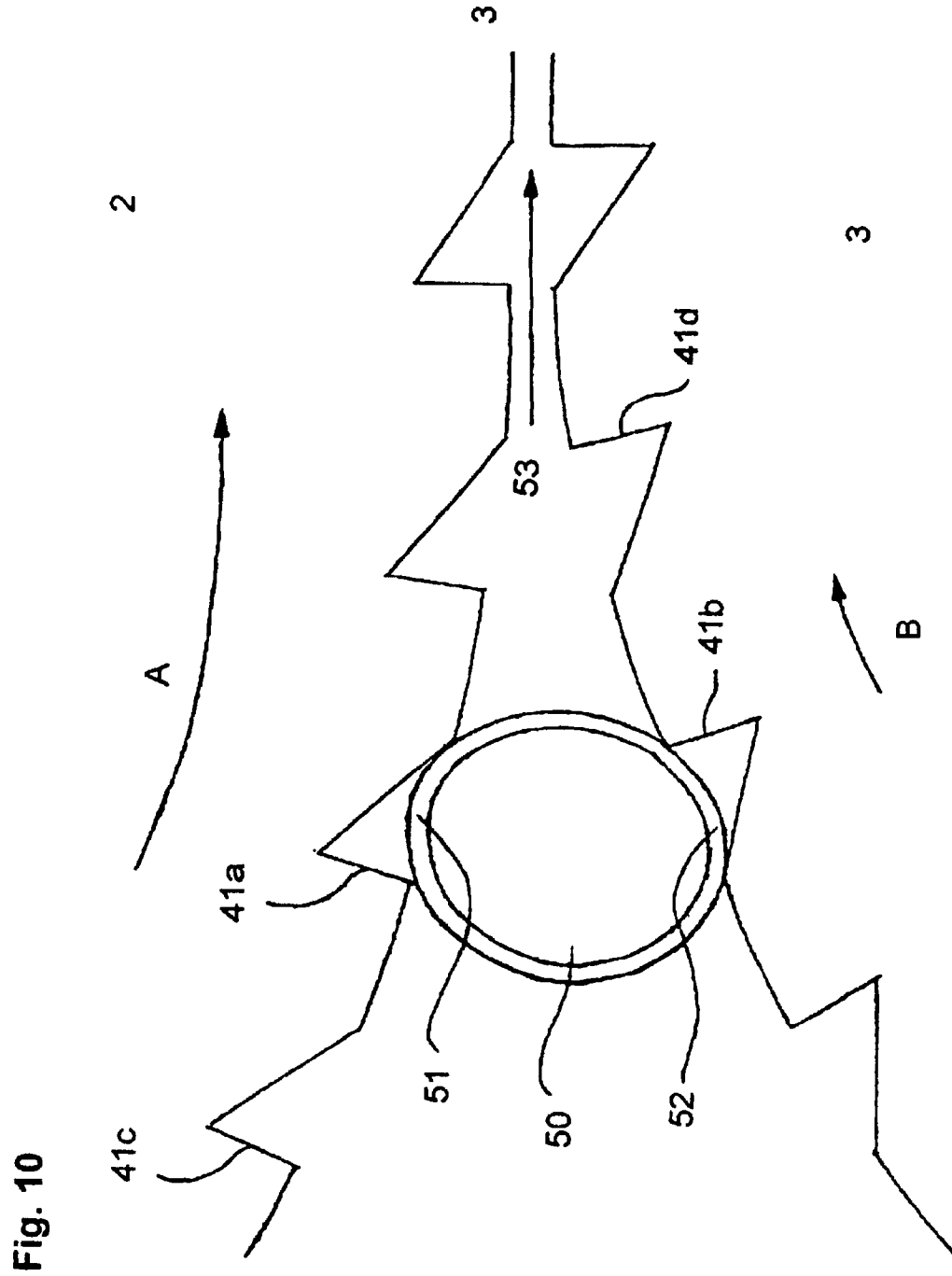


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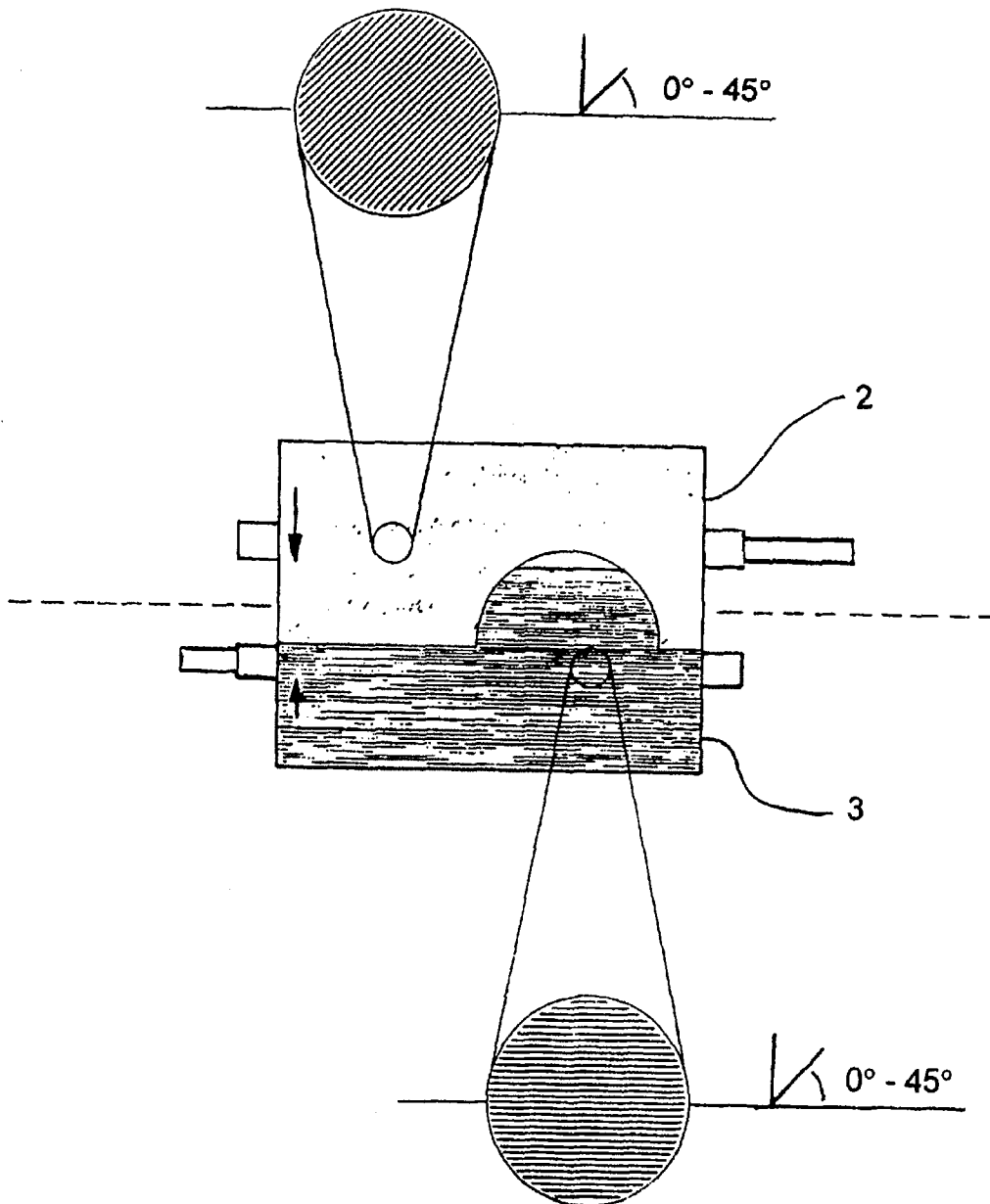
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Fig. 11



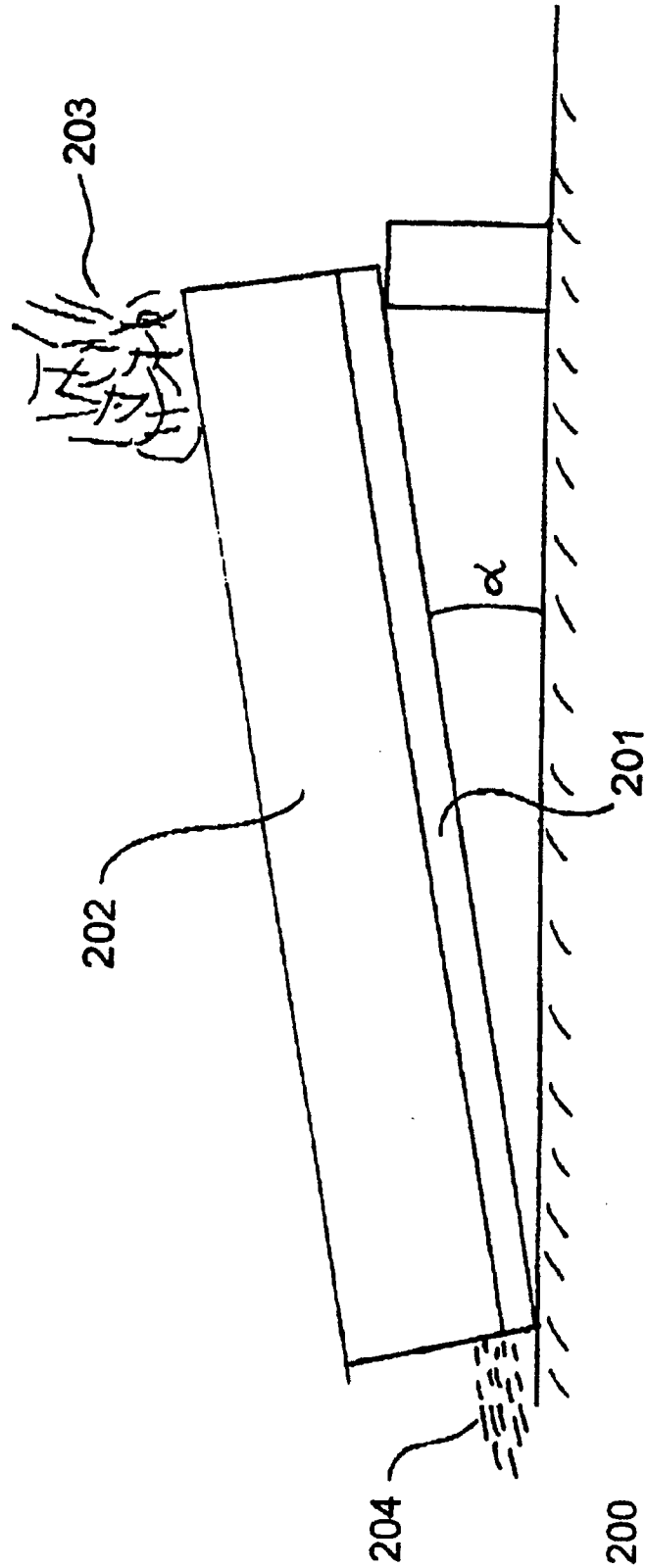
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Fig. 12



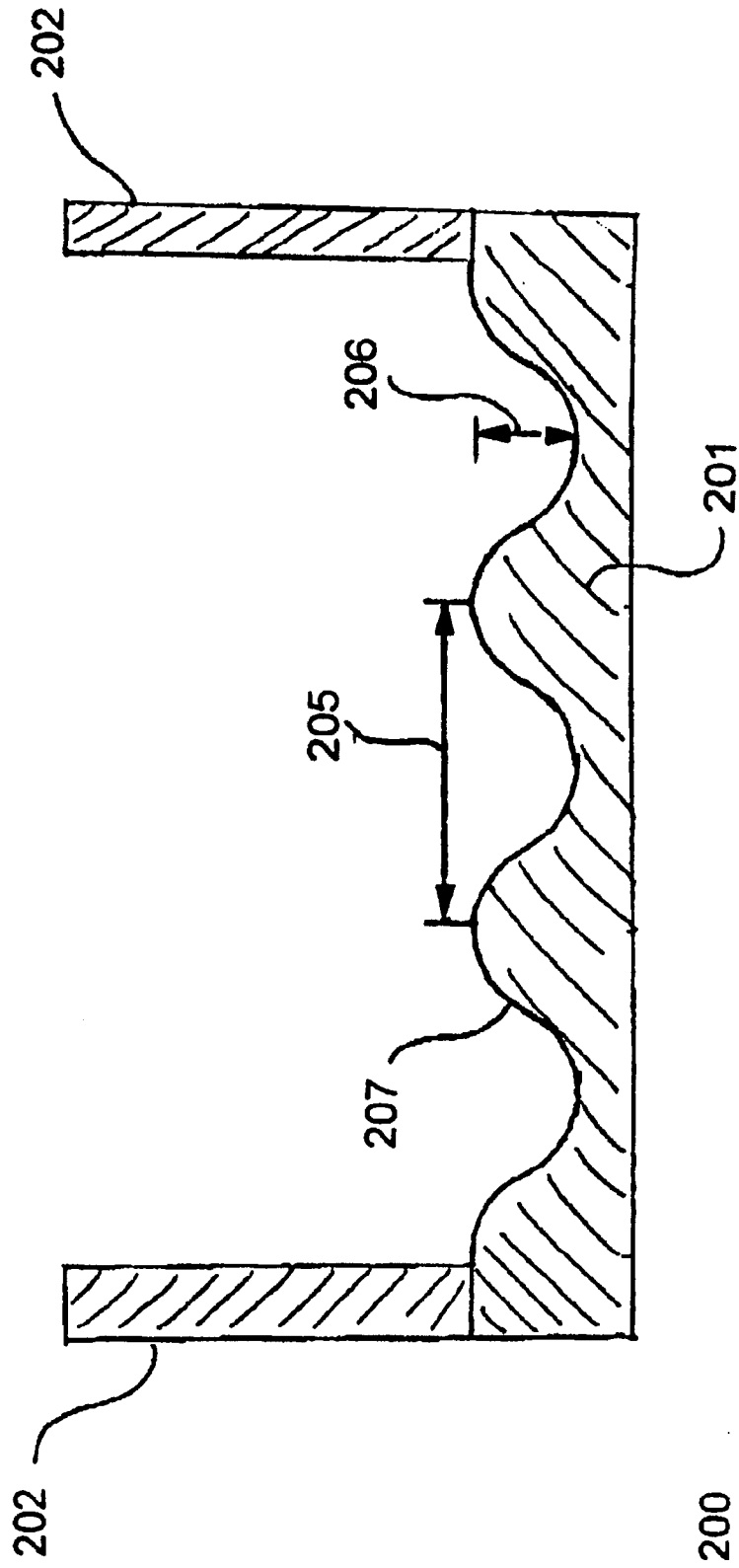
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Fig. 13



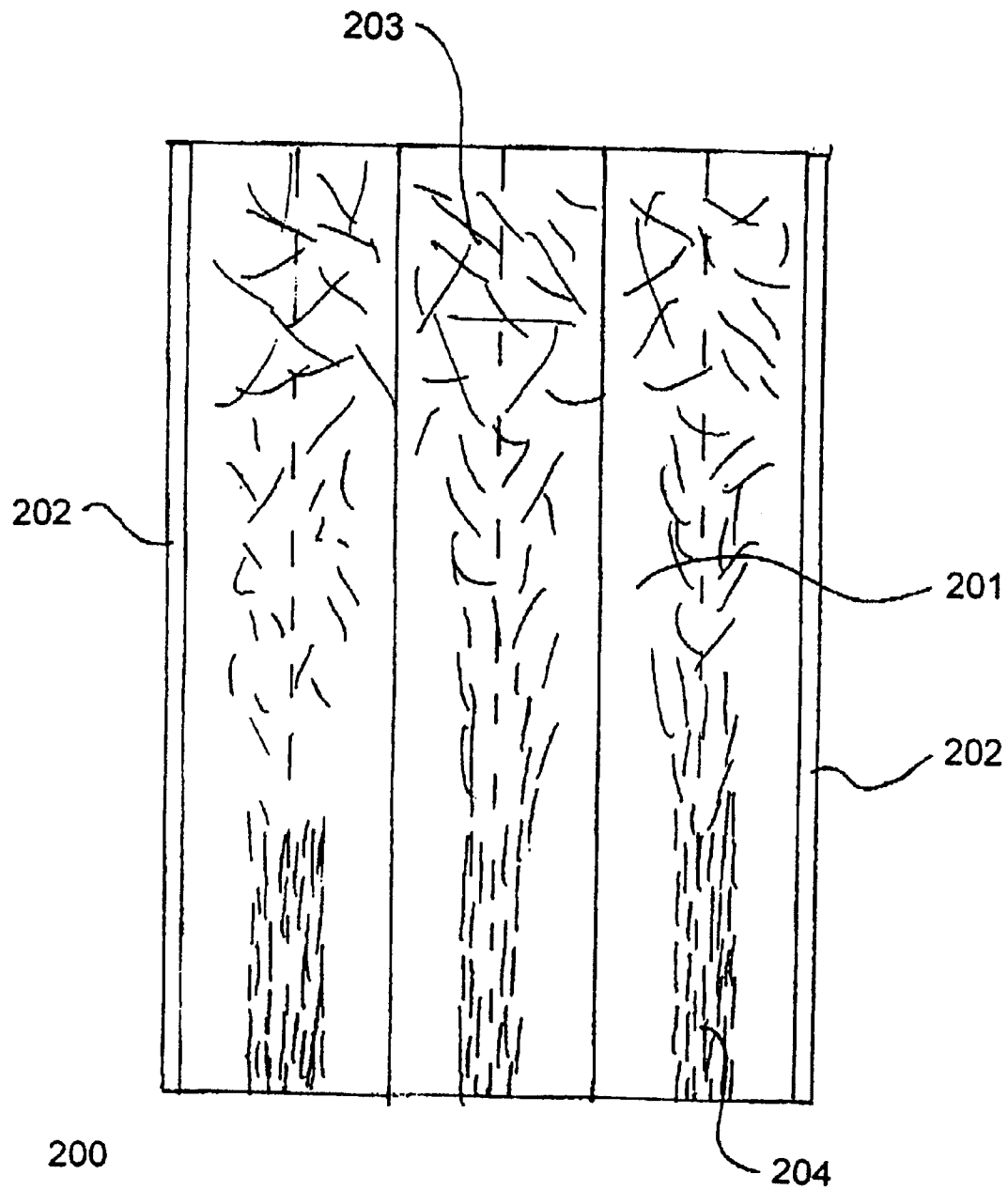
U.S. Patent

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Fig. 14



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METHOD OF FABRICATING A STRAW PANEL, BOARD, OR BEAM

FIELD OF THE INVENTION

This invention relates generally to a structural board made of straw and to a method and device for making a structural board made of straw.

BACKGROUND OF THE INVENTION

In the past, straw was not considered a suitable structural material. Unlike wood, straw has not been considered for its strength and has not commonly been considered as a building material. Current trends in the use of straw for construction involve straw bales where dense packing and size provide necessary strength and structural support. In fact, in many countries, the use of straw for construction is not permitted due to a common conception that straw is a poor building material.

In the description that follows the term cereal straw is to encompass other lignocellulosic material that is cereal straw-like in structure, such as rice straw and bamboo. Heretofore a thin panel of compressed non-woody lignocellulosic material (i.e. straw) has been made by mixing short straw pieces with a binder. Disclosure of this thin panel is found in U.S. Pat. No. 5,498,469 in the name of Howard et al. issued Mar. 12, 1996, incorporated herein by reference. The panel is used as a core layer or core stock in a plywood laminate; thus a thin layer of straw panel, is sandwiched between two layers or sheets of plywood. Although this thin panel ~0.10 inches appears to perform its intended function, the thin panels do not have sufficient strength as structural boards. The panels were incorporated with stronger wood laminate layers for the production of plywood.

Other references relating to fiber panel methods of manufacture and devices for making such panels are: U.S. Pat. No. 5,730,830 in the name of Hall, issued Mar. 24, 1998; U.S. Pat. No. 5,729,936 in the name of Maxwell, issued Mar. 24, 1998; and, U.S. Pat. No. 5,728,269 in the name of Kohno et al., issued Mar. 17, 1998.

It is an object of this invention, to provide a structural board that does not require expensive laminations forming wood/straw composites.

It is an object of this invention to provide a structural board comprised of straw and having a strength that far exceeds the strength of the straw panel described by Howard et al.

In accordance with this invention, a board or panel is provided wherein the majority of strands of straw are substantially oriented in a parallel fashion. The strands are combined with a binder.

In accordance with another aspect of the invention a board is provided wherein strands of straw are oriented in a predetermined fashion or wherein at least straw strands within at least a layer are oriented in a substantially predetermined fashion.

In accordance with the invention, there is provided, a panel, board, or beam, comprising:

a compressed straw elongate material having a plurality of strands, a plurality of the strands being substantially split longitudinally to allow a binder to contact some of the inside of the strands; and binder for binding the straw into a solid panel, board or beam.

In accordance with the invention, a panel, board, or beam, is provided comprising:

a compressed straw elongate material having a plurality of split strands, a plurality of the split strands being oriented in a predetermined manner; and

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isocyanate binder for binding the straw into a solid panel, board or beam.

In accordance with another aspect of the invention, there is provided, a method of fabricating a panel, board or beam comprising:

providing a plurality of strands of cereal straw;

splitting the cereal straw;

orienting the cereal straw such that a plurality of strands are substantially parallel; and,

adding binder to the cereal straw.

In accordance with the invention, there is provided, a panel, board, or beam, comprising:

a core of:

a compressed straw elongate material having a plurality of strands, a plurality of the strands being substantially split to allow a binder to contact some of the inside of the strands; and

binder for binding the straw into a solid panel, board or beam; and,

outer layers comprised of compressed strands of lignocellulose material other than straw.

In accordance with the invention a device for splitting straw is provided comprising two closely spaced shear rollers, said rollers being substantially the same size and having a diameter of substantially about 200 mm-800 mm.

In accordance with yet another aspect of the invention, a straw panel is provided bonded with MDI (DiphenylMethane Diisocyanate) resin and preferably, wherein a DPMA (DipropyleneGlycolMonomethylEtherAcetate) extender is used.

The strands preferably have a length of about 10 mm or greater, and preferably, are 50-100 mm long.

Structural, board, beams or panels can be fabricated in accordance with the teachings of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Exemplary embodiments of the invention will now be described in conjunction with the drawings, in which:

FIG. 1 is a graph comparing the bending ratio of a random oriented straw strand board (ROSSB) and an oriented straw strand board (OSSB);

FIG. 2 is a graph of the modulus of rupture, and modulus of elasticity versus the average split straw strand length;

FIG. 3 is a graph depicting the modulus of elasticity of waferboard made from split wheat straw;

FIG. 4 is a graph depicting the bending strength of OSSB and waferboard made from split wheat straw;

FIG. 5 is a graph depicting internal bond strength of straw panels bonded with MDI resin extended with DPMA;

FIG. 6 illustrates a side view of a straw splitter according to the invention;

FIG. 7 illustrates a side view of the opposite side of the straw splitter according to the invention shown in FIG. 6;

FIG. 8 illustrates a plan view of the straw splitter according to the invention shown in FIG. 6;

FIG. 9 illustrates a detailed view of the surface structure of the shear rollers shown in FIG. 6;

FIG. 10 illustrates the splitting process of the straw splitter according to the invention;

FIG. 11 illustrates the groove orientation on the surface of the shear rollers shown in FIG. 6;

FIG. 12 illustrates a side view of a split straw orienter according to the invention;

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FIG. 13 illustrates a cross sectional view of the split straw orienter according to the invention; and

FIG. 14 illustrates a plan view of the split straw orienter according to the invention.

DETAILED DESCRIPTION

Referring now to FIG. 1 graphs are shown comparing the bending ratio of a random oriented straw strand board ROSSB and an oriented straw strand board OSSB, wherein orientation of the strands is purposeful, and the strands are oriented so as to be substantially parallel with one another. The relative bending ratio of OSSB to ROSSB in the parallel direction is shown in these figures to be approximately 2:1, but could be as small as 1.05:1.00 and still be useful. The length of the split wheat strands used was 5 mm to 100 mm.

FIG. 2 shows the bending properties of composite straw boards made with different longitudinally split wheat straw strand length. It can be seen that as the length of the straw increases, the bending strength and stiffness increases as well.

FIG. 3 is a graph depicting the modulus of elasticity of waferboard made from split wheat straw, wherein the solid shaded columns illustrate the minimum property requirement in the Canadian code (CSA 437) for "wood-based" oriented and random oriented sectional panels.

FIG. 4 is a graph depicting the bending strength of OSSB and waferboard made from split wheat straw, wherein the solid shaded columns illustrate the minimum property requirement in the Canadian code (CSA 437) for "wood-based" oriented and random oriented sectional panels.

FIG. 5 is a graph depicting internal bond strength of straw panels bonded with MDI resin extended with DPMA.

In order to obtain maximum strength, the straw should be split, to ensure that the exterior and interior surfaces of the hollow straw stem core can be coated with a binder prior to hot pressing.

In addition to splitting the straw, it can be treated in such a manner as to at least partially strip the wax on the waxy outside stem by using a solvent. After removing the wax and splitting the straw, it becomes easier to glue and requires less glue to be used. More importantly, the finished board has greater internal bond strength. The preferred binder is MDI Isocyanate resin such as ICI's "Rubinate 1840", or Dow's "PAPI-94". Phenolic resin normally used for wood panel does not bond well to straw.

Transverse cutting or chopping of the straw can be accomplished by using a forage harvester.

Longitudinal straw cracking/splitting and node crushing can be accomplished by using one of:

- a) grooved rollers, for example a grain roller mill or a hay macerator
- b) a sander having shear action provided by equipment with rolling shear
- c) a CAE 6/36 disk waferizer ("feeding" with straw bundles rather than small logs as it is designed to be used)
- d) a CAE 12/48 ringflaker (6") with small compressed bales of straw or a
- e) a hammermill.

The combination of (a) and (e), a roller mill and a hammermill has the best results. The use of (b) and (c) is not preferred. A ringflaker (d) is useable but it has the limitation that it does not crush the node of the straw adequately.

Fines removal from split straw can be achieved by screening or air or fractionation. Once the straw has been split and

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separated, the strands must be oriented such that the strands are substantially parallel.

For strands longer than 1.0 mm moderate straw strand orientation can be achieved with minor modifications to commercially available equipment for orienting wood strands for OSB. This can also be accomplished by vibrating the strands on a corrugated panel, preferably tilted at approximately 20 degrees, or alternatively the straw strands can be dropped on parallel-aligned vertical bars placed in the form of a spaced grid with a distance less than the strand length. Shaking will then allow the straw to fall through.

For strands less than 1.0 mm, letting the strands fall between vertical oppositely charged electric condenser panels will align the straw. The dipole on the falling straw particles will align the particles parallel to the electric field. Structural panel, boards, and beams can be made in this manner, by ensuring that the longitudinal axes of the straw are aligned.

The panel, board, or beam in accordance with an aspect of this invention consists essentially of longitudinal split straw and resin binder such as MDI, wherein the straw has been oriented such that the longitudinal axes of the straw pieces are substantially parallel. It has been found that the use of DPMA (DOWANOL™) extends the coverage of MDI applied.

In another embodiment of this invention, a straw panel board is comprised of oriented strand wood board having a straw core. This embodiment has the advantage of providing a core made of lignocellulose material other than wood, where wood reserves are low, or the availability of wood is limited, while not sacrificing the structural integrity of the board. Furthermore, in some instances the appearance of wood on the outside faces of a panel board is of a commercial importance, and this embodiment meets this requirement.

In yet another embodiment of this invention, an oriented straw panel comprised of cementitious materials up to 50% (by weight), has been made. This embodiment has the advantage of providing a high degree of fire resistance combined with mechanical properties that exceeds the minimum strength requirement for wood based structural panels.

Referring to FIG. 6, a side view of a device 100 for longitudinally splitting straw for use in making a panel, board or beam according to the invention is shown. The device 100 comprises a supporting bench 1, a feed table 5 and two machine grooved shear rollers 2 and 3 oppositely driven at different rotational speeds by an electric motor 4. The straw is fed generally parallel to the roller axes using the feed table 5 angled downwardly towards the two shear rollers 2 and 3 where it is split longitudinally due to the shear action between the two shear rollers. Of course, alternatively, the roller's diameters can be varied such that they are driven at the same rotational speed but have substantially different peripheral velocity. The term peripheral velocity is used to indicate that the rollers are of the same size and are driven at different rotational speeds, or that the rollers are of different sizes and are driven at the same or different rotational speeds.

The upper shear roller 2 is affixed to the supporting bench 1, while the lower shear roller 3 is affixed to a supporting arm 6 pivoted to the bench 1 at the joint 7. The clearance between the two shear rollers is adjusted using an adjustment mechanism comprising an elevating screw 8 and a tension spring 9. Other embodiments for adjusting the clearance between the two shear rollers may be envisaged, such as a ratchet gear or rack hoisting gear. The adjustment mechanism is also used for lowering the shear roller 3 in

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case some material is stuck between the shear rollers or for cleaning purposes.

The upper shear roller 2 is driven counterclockwise at approximately 500 rpm to 1500 rpm by the speed - controlled electric motor 4 using a V - belt drive or other such drive means. The V - belt drive comprises a V - belt 10 and V - belt pulleys 11 and 12 being affixed to the axis of the electric motor 5 and the upper shear roller 2 respectively. The V - belt 10 is tightened using the primary tension lever 13. For overload protection of the electric motor 5 the V - belt pulley 11 comprises an overload clutch such as a slipping clutch. An emergency shut off is preferably also included.

Both shear rollers are made of hardened steel as a hollow cylinder of approximately 500 mm to 2000 mm in length and 200 mm to 800 mm in diameter. The shear roller surfaces comprise parallel cutting edges oriented at angles between 0° to 45° to the shear roller axis, seen in FIGS. 9 and 11. Cutting edges are machined on the exterior surface of the cylinders.

The lower shear roller 3 rotates in the opposite direction to the upper shear roller 2 at a substantially lower speed, i.e. approximately 50 rpm to 150 rpm. In order to reverse the direction of rotation and to reduce the speed a chain sprocket drive is used. The first portion of the drive comprises a V - belt pulley 14 affixed to the axis of the upper shear roller, a V - belt pulley 15 affixed to the axis of the lower shear roller and a V - belt 16. To reduce the speed the driving V - belt pulley 14 has a substantially smaller diameter than the driven V - belt pulley 15. The V - belt 16 is tightened using the secondary tensioning lever 17.

Referring to FIG. 7 the opposite side view of the device 100 is shown. The second portion of the drive comprises a sprocket 20 affixed to an axis driven by the V - belt pulley 15, a sprocket wheel 21 affixed to the axis of the lower shear roller and two supporting sprocket wheels 22 and 23. To further reduce the speed the driving sprocket wheel 20 has a substantially smaller diameter than the driven sprocket wheel 21. In order to reverse the direction of rotation the chain 24 is driven by the sprocket wheel 20 on its inside and drives the sprocket wheel 21 on its outside. The sprocket wheel 22 ensures the contact between the chain 24 and a substantial part of the circumference of the sprocket wheel 21, whereas the sprocket wheel 23 keeps the lower portion of the chain 24 from contacting the upper portion.

There are numerous other embodiments for driving the two shear rollers in opposite directions and at different speeds such as: a chain drive directly driven by the electric motor; two mating gears; two smaller electric motors each driving one shear roller using a V - belt drive; two smaller electric motors each driving directly one shear roller axis using a jaw clutch; or other arrangements obvious to persons of skill in the art.

Two shear rollers having a substantially different diameter may be used to ensure the different relative peripheral velocities of the shear rollers driven with the same rotational speed. Because the relation of the two diameters is directly proportional to the relation of the two surface speeds needed for the shear action this embodiment is limited by the feasibility of the combination of shear rollers with large differences in diameter.

Referring to FIG. 8 a plan view showing the top of the device 100 is shown. The feed table 5 is angled downwardly ending at the lower shear roller 3, which then transports the straw to the shear roller 2 for splitting. Seen more clearly in FIGS. 6 and 7, the feed table 5 is supported by a linkage 18 to the support arm 6 to follow the lower shear roller 3

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through all height adjustments. Seen more clearly in FIG. 9, the feed table 5 is directed towards the surface of the shear roller 3 ending very close to it for depositing the straw on the shear roller surface. The two shear rollers 2 and 3 are driven by the electric motor 4 using the V - belt drives on the one side of the device 100 and the chain drive on the other side. The cutting edges of the upper shear roller 2 are sharpened as required by holding a grind stone 25 to the surface of the upper shear roller 2 as it rotates in a direction opposite to which it is used. The grind stone 25 is advanced longitudinally using the adjustment mechanism 30 to contact and sharpen the cutting edges 41 along the full length of the shear roller 2. Sharpening of the lower shear roller is achieved by moving the sharpening assembly 25, 30 to the opposite side of the roller 2 on the underside of the supporting bench 1.

In front of the upper shear roller 2 a turbulence control mechanism comprising a ledge 26 having the length of the shear roller is affixed to the supporting bench 1. This ledge 26 assists in preventing the straw from being unduly blown about.

FIG. 9 shows a detailed view of the surface structure of the two shear rollers 2 and 3 rotating in opposite direction at different speeds. The straw is fed generally parallel to the axes of the shear rollers using the feed table 5. The area where the two shear rollers are closest together is enlarged to show the surfaces in detail. The clearance 40 between the two shear rollers is approximately 0.1 mm to 0.3 mm. Both shear rollers have parallel grooves 46 cut in their surfaces. These grooves have a triangular shape comprising a cutting edge 41 normal to the surface of the shear rollers whereas the opposite side 42 is at an angle of 45° to the surface of the plateau ridge 43. The groove spacing 44 is about 1.5 mm and the groove depth 45 is approximately 0.5 mm to 1.5 mm. The groove spacing 44 and the groove depth 45 are dimensioned such that they are smaller than an unsplit straw to ensure that substantially all the straw is split. The grooves 46 on shear roller 2 are arranged at an angle to the grooves 46 on shear roller 3. Numerous different shapes of the grooves may be envisaged such as the opposite side 42 of the cutting edge 41 being at an angle to the surface other than 45° or being curved. Alternatively the cutting edge 41 may have a different angle to the surface or be curved. The various shapes may also be combined differently for the two shear rollers. The cutting edge 41 of the upper shear roller 2 faces in the direction of the rotation, indicated by arrow A, and moves at about ten times the speed of the cutting edge 41 of the lower shear roller 3 which faces against the direction of the rotation, indicated by arrow B, of the lower shear roller 3.

FIG. 10 shows an unsplit straw 50 after being fed on the lower shear roller and being transported towards the opening 53 between the two shear rollers. The lower portion of the straw is sitting in a groove 46 of the lower shear roller 3, while the upper portion is caught by the cutting edge 41 of the upper shear roller 2. Due to the different orientation of the cutting edges and the different speed of the shear rollers the straw 50 is caught by the two cutting edges 41a and 41b. Consequently an upper portion 51 of the straw is cut off by the cutting edge 41a due to the shear action between the two cutting edges 41a and 41b. The remaining part of the straw 50 is further transported towards the opening 53 and is then caught by the cutting edge 41c. When the lower portion 52 of the straw 50 is cut off the remaining part of the straw 50 is then caught by the cutting edge 41d. This process is repeated until the straw 50 has passed through the opening 53 between the two shear rollers 2 and 3. The split portions of the straw are transported through the opening 53 and then released.

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FIG. 11 shows the orientation of the parallel grooves on the surface of the shear rollers. The grooves are oriented between 0° and 45° to the shear roller axis. Having a different orientation of the cutting edges for the lower 3 and the upper shear roller 2 ensures a scissor-like action to split the straw longitudinally. Advantageously, this provides long fiber pieces. FIG. 11 shows cutting edges parallel to the roller axis for the lower shear roller 3 to transport the straw 50 and cutting edges at an angle of 45° to the roller axis for the upper shear roller 2 to ensure a scissor-like longitudinal cutting. Grooves 46 parallel to the lower shear roller axis 3 allow the straw 50 which is generally aligned to the shear roller axes to be transported in the grooves 46 of the lower shear roller 3 without losing their orientation. The straw is arranged for cutting supported on its whole length by the cutting edge 41b. The straw 50 is then split by the cutting edges of the upper shear roller 2. Less force is needed for cutting the straw 50 if the cutting edge is at an angle to the shear roller axis. Cutting edges at an angle of 45° ensure splitting of the straw 50 into long fiber pieces while needing less force which translates into less power needed to drive the shear roller 3. Various different orientations of the grooves may be envisaged such as both shear rollers having grooves at an angle of 45° or any combination of angles between 0° to 45° on each of the rollers. A preferred combined angle is 45° on the top roller and 30° on the bottom roller.

Referring to FIG. 12 a side view of a split straw orienter 200 according to the invention is shown. For making a panel, board or beam according to the invention the split straw strands must be aligned prior to pressing. The randomly oriented split straw strands 203 are deposited onto a board 201 having a corrugated surface. The board is vibrated transversely. Due to the vibration the split straw strands are substantially aligned accumulating at the bottom of the grooves. Tilting the board ensures the movement of the split straw strands while being processed.

The split straw orienter 200 as shown in FIG. 12 comprises a board 201 having a corrugated surface and being tilted at an angle of approximately 10° to 45°. The board 201 is sufficiently long to assure proper alignment of the split straw strands, approximately 1500 mm to 4000 mm. Raised lateral edges or walls 202 contain the split straw within the device 200 while being processed. The randomly oriented split straw strands 203 are deposited onto the board 201 at the elevated end. The split straw orienter 200 is vibrated transversely. The transverse vibration may be realized using an electric motor and an eccentric. The aligned split straw strands 204 leave the device 200 at the lower end and may be fed on a transport belt or other means to maintain the alignment.

FIG. 13 shows a cross sectional view of the split straw orienter 200. The board 201 comprises a corrugated surface of a sine like shape having a distance 205 between two consecutive ridges of approximately 25 mm to 100 mm and a depth 206 of the grooves of approximately 20 mm to 100 mm. Alternatively, different shapes of the corrugated-like surface may be envisaged such as a triangular shape or spiked/upright walls. Affixed to the board 201 are raised lateral edges or walls 202 to contain the split straw strands within the split straw orienter 200 during the process of aligning the split straw strands. Throughout this specification, the term corrugated should be read and understood to mean corrugated or corrugated like.

Referring to FIG. 14 a plan view of the split straw orienter 200 is shown. The randomly oriented split straw 203 is

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deposited onto the board 201 at the elevated end. Due to the transverse vibration of the corrugated surface and gravitational action the split straw strands are accumulating in the grooves of the corrugated surface being aligned by the groove walls 207, seen in FIG. 13. The tilting of the board 201 ensures the movement of the split straw strands during the aligning process to the lower end of the board 201 by gravitational action.

What is claimed is:

1. A method of fabricating a panel, board or beam comprising the steps of:

providing a plurality of pieces of straw;

splitting the pieces of straw longitudinally into separated strands by passing the pieces of straw through at least two shearing rollers having cutting edges, the two rollers having substantially different circumferential speeds for providing separated longitudinal strands;

adding binder to the straw strands; and,

pressing the straw strands and allowing the binder to set.

2. A method as defined in claim 1, including the step of at least partially dewaxing a plurality of the pieces of straw.

3. A method as defined in claim 1, wherein the length of most of the straw strands provided exceed about 10 mm.

4. A method as defined in claim 1, wherein the pieces of straw are longitudinally split into separate strands and oriented such that a plurality of strands are parallel prior to adding binder.

5. A method as defined in claim 1, wherein the binder is an isocyanate resin.

6. A method as defined in claim 1, further comprising the step of adding additional lignocellulosic material other than straw to form outer layers about the pressed straw.

7. A method as defined in claim 6, wherein the added outer layers are comprised of wood.

8. A method as defined in claim 1, wherein the binder is a resin, and further comprising the step of adding an extending agent to extend the resin.

9. A method as defined in claim 1, further comprising the step of orienting the straw such that a plurality of strands are substantially parallel by placing the straw on a corrugated or corrugated-like support, and shaking the corrugated support.

10. A method as defined in claim 9, wherein the corrugated support has slots therein to allow oriented straw to pass therethrough.

11. A method as defined in claim 1, wherein the rollers are substantially the same size and having a diameter of substantially about 200 mm to 800 mm.

12. A method as defined in claim 1, wherein the rollers are knurled and wherein the clearance between the two-knurled shear rollers is substantially about 0.10 mm to 0.30 mm.

13. A method as defined in claim 1, wherein wherein respective cutting edges between the two rollers are non-parallel for providing a scissoring action upon the pieces of straw passing therethrough and for providing separated longitudinal strands.

14. A method as defined in claim 13, wherein one of the rollers in operation rotates clockwise and the other of the rollers rotates counter clockwise.

15. A method as defined in claim 14, wherein one of the rollers is rotated substantially about at least 5 times faster than the other.

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**DECLARATION OF THOMAS L. HALKOWSKI
IN SUPPORT OF CALLAWAY GOLF'S
MOTION *IN LIMINE* TO EXCLUDE
ACUSHNET'S "TEST BALLS" AND RELATED
TESTIMONY**

EXHIBIT 4



US 20040048688A1

(19) **United States**(12) **Patent Application Publication**(10) **Pub. No.: US 2004/0048688 A1****Hogge et al.**(43) **Pub. Date: Mar. 11, 2004**(54) **GOLF BALL WITH VAPOR BARRIER
LAYER AND METHOD OF MAKING SAME****Related U.S. Application Data**(76) Inventors: **Matthew F. Hogge**, New Bedford, MA
(US); **Constantine A. Kondos**,
Pittsburgh, PA (US); **Christopher**
Cavallaro, Lakeville, MA (US);
Michael D. Jordan, East Greenwich,
RI (US)(63) Continuation-in-part of application No. 09/973,342,
filed on Oct. 9, 2001, now Pat. No. 6,632,147.**Publication Classification**(51) **Int. Cl.⁷** **A63B 37/06**
(52) **U.S. Cl.** **473/361**

Correspondence Address:

Troy R. Lester**Acushnet Company****PO Box 965****Fairhaven, MA 02719-0965 (US)**(57) **ABSTRACT**(21) Appl. No.: **10/611,833**(22) Filed: **Jul. 1, 2003**

A golf ball comprising a core, a barrier layer enveloping the core, and a cover enveloping the barrier layer, wherein the barrier layer has a moisture vapor transmission rate less than that of the cover, and the barrier layer comprises a thermoplastic or thermoset composition of microparticles dispersed in a binder.

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GOLF BALL WITH VAPOR BARRIER LAYER AND METHOD OF MAKING SAME**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application is a continuation-in-part of co-pending U.S. application Ser. No. 09/973,342, filed Oct. 9, 2001, which is incorporated herein in its entirety by express reference thereto.

FIELD OF THE INVENTION

[0002] The present invention relates to golf balls, and more particularly to novel compositions and constructions for a golf ball.

BACKGROUND OF THE INVENTION

[0003] The United States Golf Association ("USGA") provides five (5) regulations to keep golf balls consistent. Specifically, the golf ball must weight no more than 1.62 ounces and measure no less than 1.68 inches in diameter. The initial velocity of the ball as test on a USGA machine at a set club head speed must not exceed 255 ft/sec. The overall distance of the ball as tested with a USGA specified driver at 160 ft/sec and a 10 degree launch angle must not exceed 296.8 yards. And the ball must pass a USGA administered symmetry test. With these guidelines, one skilled in the art can achieve certain combinations of performance characteristics (such as distance, durability, feel, spin, sound, etc.) through modifications in material compositions, constructions, and surface configurations of various portions of the ball.

[0004] Solid core golf balls are well known in the art, which are typically made from polybutadiene rubber materials that, together with high crosslink density, provide the primary source of resiliency for the golf balls. A known drawback of solid cores, such as those based on polybutadiene(s) crosslinked with peroxide and/or zinc diacrylate, is their undesirable sensitivity to and absorption of water vapor and moisture, which reduces core resiliency and degrades other ball properties, such as compression, initial velocity, and coefficient of restitution. Thus, the solid cores are usually encapsulated in a cover to shield them from the invasion of moisture and to maintain optimum ball properties. Conventional cover materials include balata (trans-polyisoprene), ionomer resins, polyurethane, and polyurea, among others. Polyurethane and polyurea covers are generally preferred for their softness, but they exhibit poor moisture barrier properties. Therefore, prolonged exposure to high humidity and elevated temperature poses a particularly significant problem to golf balls of polybutadiene solid core and polyurethane or polyurea cover.

[0005] Several prior patents have addressed the water vapor absorption problem. U.S. Pat. No. 5,820,488 discloses a barrier layer having a water vapor transmission rate lower than the cover, formed from polyvinylidene chloride, vermiculite, or a barrier-forming material disposed on the core through an in situ reaction. U.S. Pat. No. 5,875,891 discloses an impermeable packaging that limits moisture absorption by golf balls during storage. U.S. Pat. Nos. 5,885,172 and 6,132,324 disclose thin, hard ionomer-based, inner covers that offer some resistance to water vapor penetration without affecting other ball properties. U.S. Pat. No. 6,232,389

discloses a barrier layer for an air-filled or gas-filled game ball, formed from an aqueous solution of an elastomer, a dispersed exfoliated layered filler, and a surfactant. U.S. Pat. No. 6,398,668 discloses an oxygen barrier layer composed of ethylene vinyl alcohol copolymer.

[0006] However, there remains a need for other golf balls with an improved barrier layer and improved methods for applying such a barrier layer in the golf ball.

SUMMARY OF THE INVENTION

[0007] The present invention is directed to a golf ball comprising a core, a barrier layer enveloping the core, and a cover enveloping the barrier layer, wherein the barrier layer has a moisture vapor transmission rate lower than the cover. The barrier layer is formed of a thermoplastic or thermoset composition comprising microparticles, such as fibers, whiskers, metal flakes, micaceous particles, nanoparticles, or combinations thereof, dispersed in a binder comprising synthetic rubbers, natural rubbers, polyolefins, styrenic polymers, single-site catalyzed polymers, or combinations thereof. Suitable styrenic polymers include styrene-butadiene copolymers, poly(styrene-co-maleic anhydride), acrylonitrile-butylene-styrene copolymers, styrene-olefin block copolymers, poly(styrene sulfonate), and combinations thereof, with styrene-olefin block copolymers being preferred. Suitable metal flakes (preferably leafing) include aluminum flakes, iron oxide flakes, copper flakes, bronze flakes, and combinations thereof, with aluminum flakes comprising aluminum oxide being preferred. As a means for creating a hydrophobic tortuous path across the barrier layer, the microparticles have a particle size of about 4 microns to about 335 microns, and are present by about 50 phr to about 250 phr by weight of the binder. Preferably, the particle-to-binder weight ratio is about 1 to about 2.

[0008] The composition of the barrier layer can incorporate a cross-linking agent and become thermoset. Suitable cross-linking agents include polyolefin polyols, such as hydrogenated polybutadiene polyols, present in an amount of at least about 10 parts, preferably at least about 20 parts, per 100 part by weight of the binder. The composition may further comprise a catalyst, a coupling agent, or both. The coupling agent is used to bind the microparticles to the rubber binder, and/or to bond the barrier layer directly to the underlying substrate (core or layer) and/or the cover or layer disposed over the barrier layer. The barrier layer is preferably thinner than about 0.02 inches, more preferably about 0.001 inches to about 0.01 inches, and most preferably about 0.002 inches to about 0.007 inches.

[0009] Formed from these compositions, the barrier layer preferably has a moisture vapor transmission rate of less than about 0.95 grams mm/(m² day), more preferably less than about 0.65 grams-mm/(m²-day); a Sward hardness of about 5 to about 20; a pencil hardness of about 5B to about F; and a specific gravity of about 1 g/cm³ to about 1.5 g/cm³, more preferably greater than that of the core by at least about 0.1 g/cm³. Suitable methods to apply the barrier layer include spraying or dipping, where the composition is dispersed in a non-aqueous solvent system comprising aromatic hydrocarbons, ketones, acetates, alcohols, esters, or combinations thereof. This solvent-borne dispersion has a solid content of preferably at least about 15%, more preferably at least about 30%; and a viscosity of preferably about 300 cps to about 1,500 cps.

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[0010] In a preferred embodiment, the core has a diameter of at least about 1.55 inches, preferably at least about 1.62 inches; the barrier layer has a thickness of less than about 0.02 inches; and the cover has a thickness of less than 0.08 inches, preferably less than about 0.03 inches. The core can be a one-piece solid core formed from a polybutadiene having a Mooney viscosity of greater than about 35, a crosslinking agent in an amount of greater than about 15 parts per 100 parts by weight of the polybutadiene, and an optional plasticizer. The one-piece core preferably has a diameter of about 1.62 inches to about 1.64 inches, a compression of less than about 100, a deflection at 100 kg of greater than about 1.5 mm, a coefficient of restitution of greater than about 0.78, a specific gravity of less than about 1.4 g/cm³, and a peripheral hardness greater than a central hardness by at least about 5 Shore C.

[0011] Alternatively, the core comprises a center and an outer core layer enveloping the center. The center is formed from a polybutadiene having a Mooney viscosity of greater than about 35, a crosslinking agent in an amount of about 15 part to about 40 parts per 100 parts by weight of the polybutadiene, a regrind or filler, and an optional plasticizer. The center has a diameter of about 0.5 inches to about 1.6 inches, a compression of about 10 to about 100, and a deflection at 100 kg of greater than about 1.5 mm. The outer core layer, with has a material hardness of greater than about 60 Shore C, is formed from a polybutadiene having a Mooney viscosity of greater than about 35, a crosslinking agent in an amount of about 25 part to about 55 parts per 100 parts by weight of the polybutadiene, a regrind, polyisoprene, or filler, and an optional plasticizer.

[0012] The cover preferably comprises a composition formed from a thermoplastic polyurethane, a thermoset polyurethane, a thermoplastic polyurea, or a thermoset polyurea. The cover composition preferably has a material hardness of about 25 Shore D to about 65 Shore D and a flexural modulus of at least about 2,000 psi. The cover has an outermost surface occupied by preferably about 250 to about 450 dimples. The golf ball formed therefrom preferably has a compression of less than about 110, a coefficient of restitution greater than about 0.79, a moment of inertia less than about 84 g·cm², and a deflection at 100 kg of greater than about 1.5 mm.

Definitions

[0013] As used herein, the term "polyahl" or "reactive polyahl" refers to any one compound or a mixture of compounds containing a plurality of active hydrogen moieties per molecule. Illustrative of such active hydrogen moieties are —OH (hydroxy group), —SH (thio group), —COOH (carboxylic acid group), and —NHR (amine group), with R being hydrogen, alkyl, aryl, or epoxy; all of which may be primary or secondary. These active hydrogen moieties are reactive to free isocyanate groups, forming urethane, urea, thiourea or corresponding linkage depending on the particular active hydrogen moiety being reacted. The polyahls may be monomers, homo-oligomers, co-oligomers, homopolymers, or copolymers. Oligomeric and polymeric polyahls having at least one NCO-reactive group on each terminal of a backbone are typically employed as the soft segment in reaction products such as polyureas and polyurethanes. Depending on the terminal groups, the oligomeric and polymeric polyahls may be identified as polyols (with

—OH terminals only), polyamines (with —NHR terminals only), or amino alcohol oligomers or polymers (with both —OH and —NHR terminals). Such polyahls with a relatively low molecular weight (less than about 5,000), and a wide variety of monomeric polyahls, are used as curing agents. The polyahls are generally liquids or solids meltable at relatively low temperatures.

[0014] As used herein, the term "saturated" or "substantially saturated" means that the compound or material of interest is fully saturated (i.e., contains no double bonds, triple bonds, or aromatic ring structures), or that the extent of unsaturation is negligible, e.g. as shown by a bromine number in accordance with ASTM E234-98 of less than 10, preferably less than 5. Saturated compounds include compounds that are aliphatic, alicyclic, or fully hydrogenated.

[0015] As used herein, the term "percent NCO" or "% NCO" refers to the percent by weight of free, reactive, and unreacted isocyanate functional groups in an isocyanate-functional molecule or material. The total formula weight of all the NCO groups in the molecule or material, divided by its total molecular weight, and multiplied by 100, equals the percent NCO.

[0016] As used herein, the term "equivalent" is defined as the number of moles of a functional group in a given quantity of material, and calculated from material weight divided by equivalent weight, the later of which refers to molecular weight per functional group. For isocyanates the equivalent weight is (4210 grams)/% NCO; and for polyols, (56100 grams)/OH#.

[0017] As used herein, the term "flexural modulus" or "modulus" means stress to strain ratio within the elastic limit (measured in flexural mode) of a material, indicates the bending stiffness of the material, and is similar to tensile modulus. Flexural modulus, typically reported in Pascal ("Pa") or pounds per square inches ("psi"), is derived in accordance to ASTM D6272-02.

[0018] As used herein, the term "water vapor transmission rate" ("WVTR") refers to the mass of water vapor that diffuses through a material of a given thickness per unit area per unit time at a specific temperature and humidity differential. Standard tests for WVTR include ASTM E96-00, ASTM F1249-90, and ASTM F372-99, among others.

[0019] As used herein, the term "aspect ratio" refers to the ratio of a platelet particle's lateral dimension to its thickness. The term "effective aspect ratio" refers to the aspect ratio of flake particles when dispersed in a binder such as a rubber or polymer matrix. Rather than being separated as singular flakes, the flakes may exist in many forms, such as a bundle of tens or hundreds of flakes known as agglomerates. The aspect ratio of the bundle or agglomerate (i.e., the effective aspect ratio), while usually being much lower than that of the single flake, is directly related to the barrier property of the flakes in the binder.

[0020] As used herein, the term "material hardness" refers to indentation hardness of non-metallic materials in the form of a flat slab or button as measured with a durometer. The durometer has a spring-loaded indenter that applies an indentation load to the slab, thus sensing its hardness. The material hardness can indirectly reflect upon other material properties, such as tensile modulus, resilience, plasticity, compression resistance, and elasticity. Standard tests for

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material hardness include ASTM D2240-02b. Unless otherwise specified, material hardness reported herein is in Shore D. Material hardness is distinct from the hardness of a golf ball portion as measured directly on the golf ball (or other spherical surface). The difference in value is primarily due to the construction, size, thickness, and material composition of the golf ball components (i.e., center, core and/or layers) that underlie the portion of interest. One of ordinary skill in the art would understand that the material hardness and the hardness as measured on the ball are not correlated or convertible.

[0021] As used therein, the term "compression," also known as "ATTI compression" or "PGA compression," refers to points derived from a Compression Tester (ATTI Engineering Company, Union City, N.J.), a scale well known in the art for determining relative compression of a spherical object. Compression is a property of a material as measured on a golf ball construction (i.e., on-ball property), not a property of the material per se.

[0022] As used herein, the term "coefficient of restitution" or "COR" for golf balls is defined as the ratio of a ball's rebound velocity to its initial incoming velocity when the ball is fired out of an air cannon into a rigid vertical plate. The faster a golf ball rebounds, the higher the COR it has, the more the total energy it retains when struck with a club, and the longer the ball flies. The initial velocity is about 50 ft/s to about 200 ft/s, and is usually understood to be 125 ft/s, unless otherwise specified. A golf ball may have different COR values at different initial velocities.

[0023] The term "about," as used herein in connection with one or more numbers or numerical ranges, refers to all such numbers, including all numbers in a range. Because these ranges are continuous, they include any and all values between the minimum and maximum values.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Golf ball cores of the present invention may be solid, fluid-filled, or gas-filled, having a one-piece construction, two-piece construction, or multi-piece construction. The core may comprise a center and an outer core layer. The outer core layer may be an integral solid or wound layer, or discrete layers molded or wound onto each other. When two or more wound layers are present, each can be chemically, physically, or mechanically distinct from the others. Wound layer(s) are formed from threads of various sizes and materials including, but not limited to, natural rubber, polyether urea (Lycra® by DuPont), polyester urea, polyester block copolymers (Hytrel® by DuPont), polyethylene, polyamide, polyketone, poly(p-phenylene terephthalamide) (Kevlar® by DuPont), polyisoprene, among others. Wound layers may be wound at different tensions to create a hardness gradient. Suitable fluidic substances usable in fluid-filled cores include aqueous solutions, liquids, gels, rubber based gels, foams, hot-melts, pastes, colloidal suspensions, reactive liquid systems, and the like or combinations thereof. Exemplary fluidic substances include salt in water, corn syrup, glycol, oils, clay, barytes, gelatin gels, hydrogels, methyl cellulose gels, styrene-butadiene-styrene rubber in paraffinic and/or naphthenic oil, waxes, silicate gels, agar gels, peroxide cured polyester resins, epoxy resins, peroxide cured liquid polybutadiene rubbers, reactive polyurethanes or

polyureas, silicones and polyesters, SAE 10 oil, SAE 30 oil, methanol, ethanol, ammonia, glycerin, and carbon tetrachloride.

[0025] Solid cores are made from suitable core materials known to the skilled in the art, including thermoplastic and thermoset elastomers such as natural rubber, polybutadiene, polyisoprene, styrene-butadiene or styrene-propylene-diene rubber, ionomer resins, polyamides, polyesters, polyurethanes, polyureas, Pebax® from AtoFina Chemicals Inc., Hytrel® from E. I. Du Pont de Nemours and Company, and Kraton® from Shell Chemical Company. The core materials can also be formed from a castable material. Suitable castable materials include polyurethanes, polyureas, epoxies, silicones, interpenetrating polymer networks, and the like. Additionally, suitable core materials may also include a RIM polyurethane or polyurea, preferably the nucleated versions where nitrogen gas is whipped into the reaction mixture prior to injection into a closed mold to form the layer. One skilled in the art understands that other elastomers may be used as the core material without departing from the scope and spirit of the present invention.

[0026] Preferred compositions for solid cores include a base rubber, a crosslinking agent, and a free radical initiator. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is a polybutadiene having a cis-1,4 content of about 40% to about 100%, a Mooney viscosity of at least about 35, a molecular weight of at least about 150,000, and a polydispersity of less than about 4. Examples of desirable polybutadiene rubbers include Buna® CB22 and CB23 from Bayer, Ubepol® 360L and 150L from Ube Industries, and Cariflex® BCP820 and BCP824 from Shell Chemical. Blends of two or more such polybutadienes are desirable for the solid cores. In one embodiment, a cobalt or nickel catalyzed polybutadiene having a Mooney viscosity of from about 50 to about 150 is mixed with a neodymium catalyzed polybutadiene having a Mooney viscosity of from about 30 to about 100. The weight ratio between the two polybutadienes may range between about 5:95 and 95:5. The polybutadiene can also be mixed with other elastomers known in the art, such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber, in order to modify the properties of the core.

[0027] Suitable cross-linking agents for the polybutadiene-based solid cores include metal salts of unsaturated fatty acid having 3 to 8 carbon atoms, such as monoacrylate, diacrylate, monomethacrylate, and dimethacrylate. The metal can be magnesium, calcium, zinc, aluminum, sodium, lithium or nickel. Preferred cross-linking agents include zinc diacrylate, zinc dimethacrylate, and blends thereof. Zinc diacrylate is preferred because it provides golf balls with a high initial velocity, but the present invention is not limited thereto. The cross-linking agent is present in an amount of preferably at least about 15 parts per 100 parts by weight of the base polymer ("phr"), more preferably between about 15 phr and about 40 phr. In the manufacturing process, it is beneficial to pre-blend some cross-linking agent(s) with the base rubber in a master batch prior to the addition of other components.

[0028] The free radical initiator is used to promote the cross-link reaction between the base rubber and the cross-linking agent. Suitable free radical initiators include thermal initiators such as peroxide initiators, and photoinitiators

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reactive to energy sources such as UV irradiation, visible light irradiation, infrared irradiation, microwave irradiation, electron beam irradiation, x-ray irradiation, and γ -ray irradiation. Peroxide initiators are well known in the art, and can be any known peroxides or blends thereof that decompose when heated during the cure cycle. Suitable peroxide initiators include organic peroxide compounds, such as dicumyl peroxide, di-*t*-butyl peroxide, 1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, α,α -bis(*t*-butylperoxy)-diisopropylbenzene, *t*-butyl perbenzoate, 2,5-dimethyl-2,5-di(*t*-butylperoxy)-hexane, and the like or blends thereof. Commercially available examples include, but are not limited to, Varox® 231XL and DCP-R from AtoFina, Perkadox® BC and 14 from Akzo Nobel, and Elastochem® DCP-70 from Rhein Chemie. In their pure forms, the initiators are present in an amount of at least about 0.25 pph of the base polymer, preferably between about 0.5 pph and about 2.5 pph. It is understood to one skilled in the art to adjust the amount of the initiators according to their activity and concentration to affect the curing of the golf ball core.

[0029] In polybutadiene-based solid cores of the present invention, it is preferred to blend in a plasticizer, particularly a halogenated thiophenol compound such as a halogenated thiophenol or a metal salt thereof, to further enhance the softness and resiliency of the core. The halogenated thiophenol, preferably pentachlorothiophenol ("PCTP") or ZnPCTP, function in part as a *cis*-to-*trans* catalyst that convert some *cis*-1,4 bonds in the polybutadiene into *trans*-1,4 bonds. The utilization of halogenated thiophenol compounds like PCTP and ZnPCTP in golf balls to produce soft and fast cores is disclosed in co-pending U.S. patent application Ser. No. 09/951,963, which is incorporated by reference herein in its entirety. PCTP is available under the tradename of Struktol® from Struktol Company of America, and ZnPCTP is available from eChinaChem. The halogenated thiophenol compounds are present in an amount of at least about 0.1 pph of the base rubber, preferably about 0.1 pph to about 2 pph; alternatively the amount of halogenated thiophenol compound used is at least about 2 pph, preferably about 2.3 pph to about 5 pph.

[0030] The solid core may also include fillers to adjust hardness, strength, modulus, weight, density and/or specific gravity of the core. Suitable fillers include metal or alloy powders, metal oxides and salts, ceramics, particulate, carbonaceous materials, polymeric materials, glass microspheres, and the like or blends thereof. These fillers may be hollow, solid, filled, unfilled, surface treated, or non-surface treated. Specific fillers for the core include tungsten powder, tungsten carbide, zinc oxide, tin oxide, tungsten oxide, barium sulfate, zinc sulfate, barium carbonate, calcium carbonate, zinc carbonate, an array of silica and clay, regrind (recycled core material typically ground to about 30 mesh particle), and high-Mooney-viscosity rubber regrind. Certain fillers such as zinc oxide may also participate as a co-agent in the cross-link reaction of other core components.

[0031] Other optional additives for the golf ball core are well known in the art, and may be blended into the core in amounts sufficient to achieve their specific purposes and desired effects. Such additives include antioxidants to prevent the breakdown of the base polymer, accelerators to speed up the polymerization reaction, processing aids or oils to affect rheological and mixing properties, activators such as zinc stearate, foaming agents, *cis*-to-*trans* catalysts, adhe-

sives, coupling agents, lubricants, stable free radicals, radical scavengers, scorch retarders, and blends thereof.

[0032] Single-piece cores of the present invention preferably have a diameter of less than about 1.64 inches, a specific gravity of less than about 1.4 g/cm³, a compression of less than about 100, a deflection at 100 kg of greater than about 1.5 mm, a COR of at least about 0.78, and a decreasing hardness gradient from periphery to center. More preferably, the peripheral hardness of the core is greater than its central hardness by at least about 5 Shore C. Two-piece (dual) cores or multi-piece cores have different compositions and properties for the center and at least one outer core layer. The center has a ZDA level between about 15 phr and about 40 phr, incorporates at least a regrind or a filler, and optionally blends in a plasticizer like ZnPCTP. The center preferably has a diameter of about 0.5 inches to about 1.6 inches, a compression between about 10 to about 100, and a deflection at 100 kg of greater than about 1.5 mm. The outer core layer has a ZDA content between about 25 phr and about 55 phr, incorporates at least one of regrind, balata, or filler, and optionally blends in a plasticizer. The outer core layer has a material hardness of at least about 60 Shore C. The core comprising the center and the outer core layer has a diameter of less than about 1.64 inches, a compression of less than about 100, a deflection at 100 kg of greater than about 1.5 mm, and a COR of at least about 0.78. In one embodiment, the core has a diameter of greater than about 1.62 inches. Conventional methods and techniques such as compression molding are used to form the solid cores from the base compositions disclosed herein.

[0033] To prevent or minimize the penetration of moisture, typically water vapor, into the core, a barrier layer is disposed between the core and the cover, preferably immediately around the core. The barrier layer has a MVTR less than that of the cover, preferably less than about 0.95 grams-mm/(m²-day). The barrier layer of the present invention preferably comprises a thin and soft rubber layer, optionally having microparticles dispersed within a rubber material. These particles are preferably hydrophobic and create a tortuous (random and non-linear) path across the barrier layer to reduce its MVTR. The microparticles for the present invention refers to particulates that are sized on the order of several hundred microns or less, and include nanoparticles that are sized from a few nanometers to less than about 1 micron. Suitable microparticles can be pigmented or non-pigmented, and include fibers, whiskers, and flaked metals (either leafing or non-leafing), such as aluminum flakes, iron oxide flakes, copper flakes, bronze flakes, and the like or combinations of two or more thereof. Leafing metal flakes are particularly suited for use in the present invention. Preferred metal flakes include aluminum flakes and, more specifically, aluminum oxide flakes. Microparticles sized preferably about 4 microns to about 335 microns, more preferably about 5 microns to about 50 microns, and most preferably about 8 microns to about 32 microns are used. The aspect ratio of the flakes is at least about 25, and up to about 30,000, preferably about 100 to about 50 to about 20,000, more preferably about 100 to about 10,000. The amount of the microparticles present in the barrier layer is at least about 10 parts by weight per 100 parts by weight of the rubber material ("phr"), preferably between about 50 phr and about 250 phr, more preferably between about 70 phr and about 125 phr. The barrier layer may have a single layer or a plurality of sub-layers.

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[0034] The rubber material suitable for the barrier layer include, but are not limited to, synthetic or natural rubbers, such as polyolefins, styrenic polymers, single-site catalyzed polymers, acrylics, etc. Polyolefins and copolymers or blends thereof include balata, polyethylene, chlorinated polyethylene, polypropylene, polybutylene, butyl-based rubbers, isoprene rubber, trans polyisoprene, neoprene, ethylene-propylene rubber, ethylene-butylene rubber, and ethylene-propylene-(non-conjugated diene) terpolymers. Styrenic polymers include polystyrenes and copolymers thereof, such as styrene-butadiene copolymers, poly(styrene-co-maleic anhydride), acrylonitrile-butylene-styrene copolymers, styrene-olefin block copolymers (e.g. Kraton® rubbers from Shell Chemical), and poly(styrene sulfonate). Examples of styrene-olefin block copolymers are described in U.S. Pat. Nos. 4,501,842, 5,118,748, and 6,190,816. The disclosures of these patents are incorporated herein by reference in their entirety. Single-site catalyzed polymers include homopolymers and copolymers, such as grafted or non-grafted metallocene-catalyzed polyolefins. Compatibilizers may be added into the blends. The compatibilizer material is often a block copolymer where each block has an affinity for only one of the blend components to be compatibilized. The compatibilizer is thought to associate across the boundaries between phase-separated regions in the polymer blend. It is used to bind the regions together and to enhance the structural integrity and mechanical properties of the resulting compatibilized material. Optionally, these thermoplastic rubbers or blend thereof are mixed with a cross-linking agent to form a thermoset rubber material. Suitable cross-linking agents include the polymeric polyahls disclosed herein, particularly polyolefin polyols such as hydrogenated polybutadiene polyols (e.g. Polytail® H and Polytail® HA available from Mitsubishi Kasei Corp. of Tokyo, Japan, and Kraton® L-2203 available from Kraton Polymers of Houston, Tex.). The amount of the cross-linking agent is at least about 10 parts per 100 parts by weight of the rubber material, more preferably at least about 20 phr. Other additives suitable for the barrier layer include, but are not limited to, catalysts such as tertiary amines, and coupling agents such as silanes to bond the fillers to the polymer matrix. The coupling agent further enhances adhesion of the barrier layer to substrates such as a golf ball core or outer core layer, and to the layer such as a cover layer or an intermediate layer formed immediately over the barrier layer.

[0035] With the presence of the microparticles such as aluminum flakes, the barrier layer can acquire a specific gravity that is higher than that of the core, resulting in a golf ball of high moment of inertia. The barrier layer has a particle-to-binder weight ratio ("P/B") of about 0.5 to about 2.5, preferably about 1 to about 2. The barrier layer has a specific gravity of preferably about 1 g/cm³ to about 1.5 g/cm³, more preferably about 1.2 g/cm³ to about 1.35 g/cm³. The difference in specific gravity between the barrier layer and the core can be greater than about 0.1 g/cm³. The core diameter can be 1.5 inches or greater, preferably greater than about 1.55 inches, and more preferably about 1.62 inches to about 1.65 inches. Thickness of the barrier layer can be less than about 0.2 inches, but is preferably less than about 0.02 inches, more preferably about 0.001 inches to about 0.01 inches, and most preferably about 0.002 inches to about 0.007 inches. Sward hardness of the barrier layer is prefer-

ably between about 5 and about 20. Pencil hardness of the barrier layer is preferably between about 5B and about F.

[0036] The barrier layer of the present invention is preferably disposed about or embedded in any portions of a golf ball where a reduction in MVTR is desirable. Such portions include, without limitation, the core, a center within the core, an outer core layer of the core, a wound layer, an intermediate layer between the core and the cover, and an inner cover layer of the cover. Two or more barrier layers of the same or different compositions may be used in a golf ball where two or more portions have moisture absorption problems. Advantageously, each barrier layer protects a pre-selected portion of the golf ball, such that if moisture vapor penetrates an outer barrier layer, the interior layers remain protected by the inner barrier layer(s). The barrier layer is placed adjacent to the golf ball portion, covering its entire outer surface or substantially encapsulating the portion. Optionally, an adhesive or a coupling agent is used to bond the barrier layer to the portion. Alternatively, an in situ reaction takes place to form direct chemical linkages between the barrier layer and the portion. The barrier layer is preferably adjoining, more preferably contiguous, to the underlying golf ball portion. Where a liquid core is used, the moisture vapor barrier layer may serve the added function of preventing moisture vapor from exiting the liquid core to the atmosphere.

[0037] The barrier layer may be made by a number of methods. For example, the barrier layer composition may be pre-formed into semi-cured shells. Specifically, a quantity of the barrier material is placed into a compression mold and molded under sufficient pressure, temperature and time to produce semi-cured, semi-rigid half-shells. The half-shells are then place around a core or a sub-assembly and cured in a second compression mold to reach the desirable size. In a shrink-wrap method, thin sheet stock of the barrier material is placed tightly against the mold cavity wall of the upper and lower platens of a compression mold press through vacuum suction. The core or sub-assembly is inserted into the mold cavity between the sheet stock. The press is closed to compression mold and cure the barrier layer. In an injection molding method, a mixed stock of the barrier material is fed into an injection molding barrel and screw, then injected through a nozzle into a mold cavity to surround the core or sub-assembly. Heat and pressure is applied to the mold to cure the barrier layer.

[0038] A more preferred method to form the barrier layer of the present invention is spraying, in which the solid composition of the barrier layer is dispersed in a non-aqueous solvent system, and the dispersion is sprayed on golf ball precursors such as cores and then dried. Suitable solvents to disperse the binder rubber and the particles include, but are not limited to, aromatic hydrocarbons such as xylene (CAS# 1330-20-7) and toluene (CAS# 108-88-3); ketones such as methyl ethyl ketone (MEK, CAS# 78-93-3), methyl isobutyl (MIBK, CAS# 108-10-1), methyl n-amyl ketone (MAK, CAS# 110-43-0), and diisobutyl ketone (DIBK, CAS# 108-83-8); acetates such as n-butyl acetate (CAS# 123-86-4) and ethyl acetate (CAS# 141-78-6); alcohols such as n-amyl alcohol (CAS# 71-41-0); esters; or mixtures thereof. For ease of processing, the rubber materials are first dispersed in the solvents to form an intermediate with a relatively high viscosity (about 20,000 cps to about 50,000 cps) and a relatively high solid content (at least

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about 30%). The rubber intermediate is then co-dispersed with the particles in more solvents to form the sprayable dispersion having a viscosity of preferably about 300 cps to about 1,500 cps, more preferably about 500 cps to about 1,000 cps, and most preferably about 700 cps to about 900 cps. The solvent-borne sprayable dispersion has a solid content of at least about 10%, more preferably at least about 15%, and most preferably about 15% to about 40%.

[0039] Machinery setup to form the barrier layer via spraying typically uses a golf ball coater system well known to one of ordinary skill in the art. A coater line serves to spin the cores and pass them through a coating station. Within the coating station, a top spray gun and a bottom spray gun are set up to spray the top and bottom hemispheres of the cores, respectively. Both spray guns are stationary and positioned to aim at about 45 degrees from the core equator. The sprayable dispersion is placed in a pressurized pressure pot that supplies the spray guns. Sequentially, the coater line is started to move and spin the cores, and the spray guns are turned on to spray the dispersion onto the cores. Parameter ranges for each component of the coater system are detailed in the examples below.

[0040] The skilled artisans would understand to adjust various components of the coater system and their parameters for desirable results. They are also aware of other suitable manufacturing techniques for applying the dispersion of the present invention, including dipping, vacuum deposition, reaction injection molding, among others. After the application of the dispersion, the barrier layer formed therefrom becomes tack free at ambient temperature in about 5 to about 10 minutes. Preferably, the cores with the barrier layer thereon are dried, such as in a convention oven, at a temperature of about 180° F. to about 250° F. for a time period of about 10 minutes to about 60 minutes. The dry weight of the barrier layer is dependent on the solid composition of the dispersion and the size of the underlying core. Preferably, the dry weight of the barrier layer is at least about 0.3 grams per golf ball. After drying, the barrier layer may optionally undergo further surface treatment prior to the application of the cover, such as plasma, corona, silane dip, or combinations thereof.

[0041] Golf ball cover of the present invention is preferably tough, cut-resistant, and selected from conventional materials used as golf ball covers based on the desired performance characteristics. The cover may comprise one or more layers, such as an outer cover layer and one or more inner cover layer(s). Inner cover layer(s) may be wound layer(s) or hoop stress layer(s). Suitable cover materials include non-ionomeric acid copolymers, such as ethylene (meth)acrylic acid copolymers and terpolymers having an acid content of about 2% to about 50%, under the trade names of Nucrel® from E. I. DuPont de Nemours & Company and Escor® from ExxonMobil; anionic and cationic ionomers, such as the acid copolymers partially or fully neutralized with organic or inorganic cations by about 1% to about 100% or more, under the trade names of Surlyn® from E. I. DuPont de Nemours & Company and Iotek® from ExxonMobil; thermoplastic or thermoset (vulcanized) synthetic or natural rubbers, such as polyolefins and copolymers or blends thereof, polystyrenes and copolymers thereof, and polymers produced with single-site catalysts such as metallocene; thermoplastic or thermoset polyurethanes; thermoplastic or thermoset polyureas; aliphatic or

aromatic thermoplastics, such as polyesters (Hytrel® from E. I. DuPont de Nemours & Company and Lomod® from General Electric Company), polycarbonates, polyacetals; polyimides, polyetherketones, polyamideimides, block copolymers (Kraton® rubbers from Shell Chemical), and co-polyetheramides (Pebax® from AtoFina); vinyl resins such as polyvinyl alcohol copolymers and PVDC; polyamides such as poly(hexamethylene adipamide) and others prepared from diamines, fatty acids, dibasic acids, and amino acids; acrylic resins; synthetic or natural vulcanized rubber such as balata; and blends and alloys, such as blends of polycarbonate and acrylonitrile-butylene-styrene, blends of polycarbonate and polyurethane, and blends of polyvinyl chloride with acrylonitrile-butadiene-styrene or ethylene vinyl acetate.

[0042] Preferably, the golf ball cover comprises a polyurethane or polyurea composition having a reaction product formed from a polyah, an isocyanate, and an optional curing agent. The polyahs are preferably incorporated into one or more soft segments of the reaction product, and are substantially absent in any hard segments. Suitable polyahs such as polyols and polyamines are organic, modified organic, saturated, aliphatic, alicyclic, unsaturated, araliphatic, aromatic, substituted, unsubstituted, or ionomeric, having two or more reactive hydrogen groups per molecule, such as primary or secondary hydroxy groups or amine groups. The isocyanate-reactive hydroxy and/or amine groups may be terminal or pendant groups on the oligomeric or polymeric backbone, and in the case of secondary amine groups, may even be embedded within the backbone.

[0043] Any isocyanate available to one of ordinary skill in the art is suitable for use according to the invention. The isocyanate may be organic, modified organic, saturated, aliphatic, alicyclic, unsaturated, araliphatic, aromatic, substituted, or unsubstituted diisocyanate or polyisocyanate monomers having two or more free reactive isocyanate ("NCO") groups; isomers thereof; modified derivatives thereof; dimers thereof; trimers thereof; or isocyanurates thereof. The isocyanate may also include any isocyanate-terminated multimetric adducts, oligomers, polymers, prepolymers, low-free-monomer prepolymers, quasi-prepolymers, and modified polyisocyanates derived from the isocyanates and polyisocyanates above. Low-free-monomer prepolymers refer to prepolymers having free isocyanate monomer levels less than about 0.5 weight percent. Curing agents are monomeric, oligomeric, or polymeric compounds used in cover compositions for chain-extension and/or crosslink. Suitable curing agents for the invention include polyahs and epoxies, preferably hydroxy curatives, amine curatives, and amino alcohol curatives having a molecular weight of about 50 to about 5,000.

[0044] For best light stability, all reactants in the polyurethane or polyurea compositions, including the polyah(s), the isocyanate(s), and the curing agent(s) are substantially saturated. A hindered secondary diamine having a high level of stearic hindrance, such as Clearlink® 1000 (4,4'-bis(sec-butylamino)-dicyclohexylmethane) from Dorf Ketal Chemicals LLC, may be used to beneficially slow down the curing process.

[0045] A variety of additives can optionally be incorporated into the cover layer compositions of the present

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invention in amounts sufficient to achieve their specific purposes and desired effects. For example, a catalyst such as dibutyltin dilaurate (Dabco® T-12), in an amount of about 0.001 weight percent to about 5 weight percent of the total formulation, may be employed to promote the reaction between the curing agent and the prepolymer. UV absorbers, light stabilizers (preferably hindered amine light stabilizers), and antioxidants are used to prevent cover yellowing and surface fractures due to photo-degradation. Other additive include, but are not limited to, accelerators, fillers, viscosity modifiers, release agents, plasticizers, compatibilizing agents, coupling agents, dispersing agents, colorants including pigments and dyes, optical brighteners, surfactants, lubricants, stabilizers, metals, processing aids or oils, blowing agents, freezing point depressants, and any other modifying agents known to one of ordinary skill in the art. Dispersing agents can be anionic, cationic, and nonionic, including materials otherwise known as leveling agents, emulsifiers, anti-foaming agents, wetting agents, surfactant, etc. Pigments may be fluorescent, autofluorescent, luminescent, or chemoluminescent, and include white pigments such as titanium oxide and zinc oxide. Fillers are used to adjust properties such as density or specific gravity, flexural modulus, tensile modulus, strength, moment of inertia, hardness, abrasion resistance, weatherability, volume, weight, etc. The fillers are preferably in the forms of nano-scale or micro-scale powders, fibers, filaments, flakes, whiskers, wires, tubes, or particulates for homogenous dispersion.

[0046] The cover layer preferably has a flexural modulus of at least about 2,000 psi, a material hardness between about 25 Shore D and about 65 Shore D, and a hardness as measured on the ball of less than about 80 Shore D. In one embodiment, the cover layer has a Shore D hardness of about 30 to about 60 and a flexural modulus of about 10,000 psi to about 80,000 psi. A thin cover layer with a thickness of about 0.01 inches to about 0.04 inches is preferred for players with high swing speeds, while a relatively thick cover layer of greater than 0.04 inches to about 0.08 inches, more preferably about 0.05 inches to about 0.07 inches, is preferred for players with moderate swing speeds. The later benefits from a golf ball of the present invention, having a high energy, large PBD core for distance off the tee and more spin, feel, and playability for greenside play from a relatively thick thermoset polyurethane or polyurea cover, without the moisture absorption problem normally associated with conventional urethane covered, PBD core golf balls. In a preferred embodiment, the cover thickness is less than 0.03 inches.

[0047] Any method known to one of ordinary skill in the art may be used to produce the cover layer of the present invention. One-shot method involving concurrent mixing of the isocyanate, the polyether polyol, and the curing agent is feasible, but the resulting mixture is non-homogenous and difficult to control. The prepolymer method described above is most preferred, because it affords a more homogeneous mixture resulting in a more consistent polymer composition. The prepolymer may be reacted with a diol or a secondary diamine to form a thermoplastic material, or reacted with a triol, tetraol, primary diamine, triamine, or tetramine to form a thermoset material. Other methods suitable for forming the layers include casting, compression molding, reaction injection molding ("RIM"), liquid injection molding ("LIM"), injection-compression molding, pre-reacting the components to form an injection moldable thermoplastic material

and then injection molding, and combinations thereof, such as RIM/compression molding, injection/compression molding, progressive compression molding, and the like. Thermoplastic formulations may be processed using any number of compression or injection molding techniques. Thermoset formulations may be castable, reaction injection moldable, sprayable, or applied in a laminate form or by any techniques known in the art. Castable reactive liquid materials such as polyurea, polyurethane, and polyurethane/polyurea hybrid can provide very thin layers such as outer cover layers that are desirable on golf balls. Other techniques include spraying, dipping, spin coating, or flow coating methods.

[0048] An optional intermediate layer may be disposed between the core and the cover, preferably between the cover and the barrier layer. The intermediate layer may be part of the core as an outer core layer, or part of the cover as an inner cover layer. The intermediate layer of the golf ball may be formed from non-ionomeric acid polymers or ionomeric derivatives thereof, polyamides, polyolefins, polyurethanes, polyureas, epoxies, polyethers, polyesters, polyetheresters such as Hytrel® from DuPont, polyetheramides such as Pebax® from AtoFina, nylons, metallocene-catalyzed polymers, styrenic block copolymers such as Kraton® from Shell Chemicals, acrylonitrile-butadiene-styrene copolymers ("ABS"), polyvinyl chlorides, polyvinyl alcohol copolymers, polycarbonates, polyesteramides, polyamides, polyimides, polyetherketones, polyamideimides, silicones, metal salts of fatty acids, and combinations thereof, such as blends of polycarbonate and acrylonitrile-butadiene-styrene, blends of polycarbonate and polyurethane. Two or more of these materials may be blended together to form the intermediate layer.

[0049] The intermediate layer may incorporate a modulus-enhancing filler or a density-modifying filler to attain preferred physical and mechanical properties. The composition of the intermediate layer may have a modulus of about 1,000 psi to about 150,000 psi, a material hardness of about 20 Shore C to about 80 Shore D, and a thickness of about 0.005 inches to about 0.6 inches. The composition of the intermediate layer may be applied as a liquid, powder, dispersion, lacquer, paste, gel, melt, or solid half shells. The intermediate layer may be formed around the core or onto the inside of the cover by sheet stock or vacuum shrink-wrapping, compression molding, injection molding, vacuum deposition, RIM, lamination, casting, spraying, dipping, powder coating, or any other deposition means. Preferably, a combination of these methods is used, such as injection/compression molding, RIM/compression molding, pre-form/compression molding, injection molding/grinding, injection/progressive compression molding, co-injection molding, or simplified casting of a single block material.

[0050] The resulting golf ball, including the core, the barrier layer, the optional intermediate layer, and the cover as described above, preferably has a COR of greater than about 0.79, a compression of less than about 110, a moment of inertia of less than about 84 g-cm², and a deflection at 100 kg of greater than about 1.5 mm. The golf ball preferably has an overall diameter of at least about 1.68 inches, more preferably from about 1.68 inches to about 1.76 inches. In a preferred embodiment, a polyurethane or polyurea cover is disposed immediately about the barrier layer so that the two are contiguous with each other. The coupling agent used in

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the barrier layer with its functionality forms direct linkage with components of the cover, thereby substantially enhances the adhesion between the two layers. At least 60% of the outermost surface of the golf ball is covered by about 250 to about 450 dimples of equal or different shape and size. Preferred dimple patterns involving catenary curves, and preferred lift and drag characteristics of the golf ball of the present invention are disclosed in co-pending U.S. application Ser. Nos. 09/989,191 and 10/096,852, respectively, both incorporated herein by reference in their entirety.

[0051] The barrier layers of the present invention and their application in golf balls are further illustrated in the following non-limiting examples. Exemplary barrier layer compositions, available from PPG industries, Inc. of Pittsburgh, Pa., are listed below in Table I.

TABLE I

Formula	Composition		P/B	Sward Hardness	Pencil Hardness
	Particle	Binder			
02-005-94D	50 parts E30B ¹	100 parts FG1901X ²	0.5	14	HB
02-005-94C	75 parts E30B	100 parts FG1901X	0.75	10	B
02-005-94A	100 parts E30B	100 parts FG1901X	1.0	12	2B
02-005-93A	80 parts E30B	80 parts FG1901X; 20 parts Polytail H ³	0.8	8	4B
02-005-81A ⁴	200 parts E30B	80 parts FG1901X; 20 parts Polytail H	2.0	6	5B
02-005-108A	100 parts E30B	100 parts FG1901X	1.0	12	2B

¹E30B is a specie of aluminum-based leafing flakes, with an averaged particle size of about 13 microns, available from ECKART America of Painesville, OH.

²FG1901X is a Kraton® rubber from Shell Chemical of Houston, TX.

³Polytail™ H is a cross-linking agent from Mitsubishi Kasei Corporation of Tokyo, Japan.

⁴This composition further includes 2.5 parts of a tertiary amine catalyst (Armeen® DM12D from Albemarle Corporation of Baton Rouge, LA) and 0.7 parts of a coupling agent (Silquest® A-1100 from Crompton Corporation - OSI Specialties of South Charleston, WV)

[0052] To form Formula 02-005-108A, a 1-gallon intermediate of Kraton® FG1901X in a solvent blend of 75% toluene and 25% MIBK with a solid content of about 33% was first formed to ease the processing. With Cowles agitation, 900 grams of Kraton® FG1901X resin (in bead form) was slowly mixed into a solvent blend of 1,350 grams of toluene and 450 grams of MIBK in a 1-gallon container, and then dissolved using high speed agitation. Since the shearing action of the Cowles blade could heat up the flammable solvent blend, as a precaution, the solvent temperature was controlled to below about 140° F. using, for example, a water jacket or air cooling. The Kraton® intermediate had a viscosity of about 28,000 cps to about 35,000 cps at about 24° C. Also with Cowles agitation, 615.2 grams of Eckart® E30B leafing aluminum pigment with a solid content of about 65%, which comprised 400 grams of leafing flakes, was slowly and thoroughly mixed into a solvent blend of 640 grams of Aromatic 100 (CAS# 64742-95-6) and 160 grams of MIBK in another 1-gallon container. The mixing typically took about 15 minutes at medium agitation, until no agglomerates or flocculated flakes was visible along the side wall of the container. Then, 1,200 grams of the Kraton® intermediate was slowly mixed in for another 15 minutes at medium agitation speed. As a result, the formula 02-005-108A had a P/B of 1.0.

[0053] To form the barrier layer over the core, the gallon-sized container with the Formula 02-005-108A therein was first placed on a paint shaker for about 7 minutes to ensure homogeneity of the sprayable dispersion, and then placed in a sealed pressure pot. Preferably the pressure pot had stirring capability to keep the dispersion homogenous. Viscosity of the 02-005-81A composition was measured to be in the range of about 600 cps to about 850 cps. This dispersion did not require further dilution prior to application, and was used at ambient temperature. The particular spray guns used were Binks® Model 95AR pneumatically activated spray guns available from ITW Industrial Finishing of Glendale Heights, Ill., in combination with spray nozzles 68PB, fluid nozzles 68SS (2.8 mm orifice diameter), and needle stems 768. Alternatively, the same spray gun can be used in

combination with spray nozzles 67PB, fluid nozzles 67SS (2.2 mm orifice diameter), and needle stems 767. Various parameters of the pressure pot, the coater line, the top spray gun, and the bottom spray gun used in preparing golf ball precursors of Groups 1-3 are listed in Table II below.

TABLE II

Component	Parameter	Value
Coater Line	Line speed	~60 balls per minute
	Spin rate	~300 rpm
Pressure Pot	Pressure	40 psi
Top Spray Gun	Open clicks	25 clicks from open position
	Fan Pattern	Half open
	Atomization air pressure	50 psi (45 psi triggered)
	Fluid flow rate	375 cm ³ /min
Bottom Spray Gun	Open clicks	60 clicks from open position
	Fan Pattern	Full open
	Atomization air pressure	50 psi (45 psi triggered)
	Fluid flow rate	300 cm ³ /min

[0054] To form the formula 02-005-81A, a Kraton® FG1901X intermediate with a solid content 20 of about 16.7% was first made by mixing and dissolving 400 grams of Kraton® FG1901X resin in bead form into 2,000 grams of toluene under high speed Cowles agitation in a 1-gallon

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container. A Polytail™ H intermediate with a solid content of 10.8% was also made by dissolving 300 grams of Polytail™ H with stirring into 2,476.5 grams of toluene in a 5-liter flask. The flask was heated to 95° F., and then to 130° F. over 3 hours. The Polytail™ intermediate was stirred for another 2 hours at 130° F. before cooling down to room temperature, after which it was filtered through a 5-micron bag into a 1-gallon container. Then, 461.4 grams of the Eckart® E30B leafing aluminum pigment was mixed with 663 grams of the Kraton® intermediate and 277.7 grams of the Polytail™ intermediate in a separate 1-gallon container. About 30 minutes of medium Cowles agitation was sufficient to disperse the leafing aluminum agglomerates into the solvent-resin blend. This was followed by slow addition of 3.75 grams of Armeen® DM12D and 1.05 grams of Silquest® A-1100. A significant increase in viscosity ensued in less than about 30 seconds. Finally, 1,350 grams of toluene was added to result in Formula 02-005-81A having a P/B of about 2 and a solid content of about 16%.

[0055] To demonstrate application of the barrier layer, five groups of golf ball precursors were constructed. Core group included twelve polybutadiene-based cores of about 1.55 inches in diameter. Groups 1, 2, and 3 each included twelve precursors having a core as the core group encapsulated in a barrier layer formed of Formula 02-005-81A with a thickness of about 0.0035 inches, about 0.0045 inches, and about 0.0069 inches, respectively. Control group included twelve precursors having a core as the core group encapsulated in a Surlyn® ionomer mantle layer of about 0.035 inches thick. Formula 02-005-81A provided a MVTR of less than about 0.65 grams-mm/(m²-day).

[0056] To demonstrate weight changes and concomitant compression changes due to moisture uptake, all five groups were subjected to three consecutive cycles of exposure in a humidity box at about 100% humidity and about 100° F. The results following each cycle are reported in Table III below, which show that the barrier layer of various thicknesses is effective in reducing weight gain and compression increase due to water vapor absorption in PBD-based golf ball cores. The barrier layer provides a reduction in core moisture uptake of at least about 30%, preferably at least about 50%, and more preferably greater than about 60%, in comparison with bare cores. The thin barrier layer more impervious to water vapor than the relatively thick ionomer layer, with a reduction in moisture uptake of at least about 20%, preferably at least about 40%. The concomitant reduction in compression increase, as provided by the barrier layer of the invention, ranges from about 20% to about 60% with respect to bare cores.

TABLE III

	Post-Cycle ΔCompression	Cumulative ΔCompression	Post-Cycle ΔWeight (g)	Cumulative ΔWeight (g)
Cycle I - 17 days				
Core	10	10	0.26	0.26
Group 1	4	4	0	0
Group 2	5	5	-0.03	-0.03
Group 3	8	8	-0.12	-0.12
Control	0	0	0.08	0.08

TABLE III-continued

	Post-Cycle ΔCompression	Cumulative ΔCompression	Post-Cycle ΔWeight (g)	Cumulative ΔWeight (g)
Cycle II - 20 days (cumulative 37 days)				
Core	6	16	0.15	0.40
Group 1	5	9	0.06	0.06
Group 2	5	10	0.04	0.01
Group 3	4	11	0.01	-0.11
Control	4	4	0.06	0.13
Cycle III - 34 days (cumulative 71 days)				
Core	4	20	0.17	0.56
Group 1	1	11	0.09	0.16
Group 2	1	12	0.08	0.12
Group 3	1	13	0.05	0.05
Control	1	4	0.09	0.20

[0057] In one particular example, a two-piece golf ball includes a core, a cover, and a barrier layer of the present invention between the core and the cover. The core is formed of a polybutadiene having a Mooney viscosity of greater than about 35, an initiator, and a ZDA level of about 15 phr or greater. Optionally, the core incorporates ZnPCTP. The core has a diameter of less than about 1.64 inches, a specific gravity of less than about 1.4 g/cm³, a compression of less than about 100, a deflection at 100 kg of greater than about 1.5 mm, and a COR of greater than about 0.78. The core is harder on the outside than on the inside, with a peripheral hardness greater than a central hardness by at least about 5 Shore C. The barrier layer is formed of a particle dispersed in a binder, with a P/B of about 1 to about 2. Preferably, the particle is leafing flakes of aluminum, more preferably aluminum oxide, and the binder includes a styrenic rubber such as Kraton® by Shell Chemicals. The barrier layer has a thickness of less than about 0.02 inches, and a MVTR less than that of a Surlyn® by DuPont. The cover is formed of a thermoplastic or thermoset polyurethane or polyurea, having a material hardness of about 25 Shore D to about 65 Shore D, and a flexural modulus of greater than about 2,000 psi. Preferably, the cover is directly adhered to the barrier layer through a coupling agent incorporated in the barrier layer. The resulting golf ball is covered with about 250 to about 450 dimples, and has a compression less than about 110, a deflection at 100 kg greater than about 1.5 mm, a moment of inertia less than about 84 g-cm², and a coefficient of restitution greater than about 0.79.

[0058] In another example, a three-piece golf ball includes a dual core, a cover, and a barrier layer between the dual core and the cover. The dual core is formed of a center and an outer core layer disposed about the center. The center includes a polybutadiene with a Mooney viscosity of greater than about 35, an initiator, and a ZDA level of about 15 phr to about 40 phr. The center further incorporates a regrind or filler such as tungsten metal powder. The center has a diameter of about 0.5 inches to about 1.6 inches, a compression of about 10 to about 100, and a deflection at 100 kg of greater than about 1.5 mm. The outer core layer includes a polybutadiene with a Mooney viscosity of greater than about 35, an initiator, and a ZDA level of about 25 phr to about 55 phr. The outer core layer further incorporates a regrind, a polyisoprene such as balata, or a filler such as tungsten metal powder. Optionally, the center, the outer core layer, or both can incorporate ZnPCTP. The resulting dual

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core has a diameter of less than about 1.64 inches, a compression of less than about 100, a deflection at 100 kg of greater than about 1.5 mm, a peripheral hardness of greater than about 60 Shore C, and a COR of greater than about 0.78. The barrier layer is formed of a particle dispersed in a binder, with a P/B ratio of about 1 to about 2. Preferably, the particle is leafing flakes of aluminum, more preferably aluminum oxide, and the binder includes a styrenic rubber such as Kraton® by Shell Chemicals. The barrier layer has a thickness of less than about 0.02 inches, and a MVTR less than that of a Surllyn® by DuPont. The cover is formed of a thermoplastic or thermoset polyurethane or polyurea, having a material hardness of about 25 Shore D to about 65 Shore D, and a flexural modulus of greater than about 2,000 psi. Preferably, the cover is directly adhered to the barrier layer through a coupling agent incorporated in the barrier layer. The 3-piece golf ball is covered with about 250 to about 450 dimples, and has a compression less than about 110, a deflection at 100 kg greater than about 1.5 mm, a moment of inertia less than about 84 g·cm², and a coefficient of restitution greater than about 0.79.

[0059] All patents and patent applications cited in the foregoing text are expressly incorporated herein by reference in their entirety.

[0060] The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended solely as illustrations of several aspects of the invention. Any equivalent embodiments and various modifications apparent to those skilled in the art are intended to be within the scope of this invention. It is further understood that the various features of the present invention can be used singly or in combination thereof. Such modifications and combinations are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball comprising a core, a barrier layer enveloping the core, and a cover enveloping the barrier layer, wherein:

the barrier layer has a moisture vapor transmission rate less than that of the cover; and

the barrier layer comprises a thermoplastic or thermoset composition of microparticles dispersed in a binder comprising synthetic rubbers, natural rubbers, polyolefins, styrenic polymers, or single-site catalyzed polymers.

2. The golf ball of claim 1, wherein the binder comprises a styrenic polymer comprising styrene-butadiene copolymers, poly(styrene-co-maleic anhydride), acrylonitrile-butylene-styrene copolymers, styrene-olefin block copolymers, or poly(styrene sulfonate).

3. The golf ball of claim 2, wherein the styrenic polymer comprises at least one styrene-olefin block copolymer.

4. The golf ball of claim 1, wherein the microparticles comprise fibers; whiskers; metal flakes; micaceous particles; or nanoparticles.

5. The golf ball of claim 4, where the metal flakes comprises aluminum flakes; iron oxide flakes; copper flakes; or bronze flakes.

6. The golf ball of claim 5, where the aluminum flakes comprise aluminum oxide.

7. The golf ball of claim 1, wherein the microparticles have a particle size of about 4 microns to about 335 microns.

8. The golf ball of claim 1, wherein the microparticles are present in an amount of about 50 parts to about 250 parts per 100 parts by weight of the binder.

9. The golf ball of claim 1, wherein the composition has a particle-to-binder weight ratio of about 1 to about 2.

10. The golf ball of claim 1, wherein the binder is thermoset and further comprises a cross-linking agent.

11. The golf ball of claim 10, wherein the cross-linking agent comprises a polyolefin polyol comprising hydrogenated polybutadiene polyols.

12. The golf ball of claim 11, wherein the cross-linking agent is present in an amount of at least about 10 parts per 100 part by weight of the binder.

13. The golf ball of claim 11, wherein the cross-linking agent is present in an amount of at least about 20 parts per 100 part by weight of the binder.

14. The golf ball of claim 1, wherein the composition further comprises a catalyst or a coupling agent.

15. The golf ball of claim 14, wherein the barrier layer is directly bonded to the cover through the coupling agent.

16. The golf ball of claim 1, wherein the barrier layer has a thickness of about 0.001 inches to about 0.01 inches.

17. The golf ball of claim 1, wherein the barrier layer has a thickness of about 0.002 inches to about 0.007 inches.

18. The golf ball of claim 1, wherein the barrier layer has a moisture vapor transmission rate of less than about 0.95 grams-mm/(m²·day).

19. The golf ball of claim 1, wherein the barrier layer has a moisture vapor transmission rate of less than about 0.65 grams-mm/(m²·day).

20. The golf ball of claim 1, wherein the barrier layer has a Sward hardness of about 5 to about 20.

21. The golf ball of claim 1, wherein the barrier layer has a pencil hardness of about 5B to about F.

22. The golf ball of claim 1, wherein the barrier layer has a specific gravity between about 1 g/cm³ and about 1.5 g/cm³.

23. The golf ball of claim 1, wherein the barrier layer has a specific gravity greater than that of the core by at least about 0.1 g/cm³.

24. The golf ball of claim 1, wherein the composition is dispersed in a non-aqueous solvent system comprising aromatic hydrocarbons, ketones, acetates, alcohols, or esters.

25. The golf ball of claim 24, wherein the solvent-borne dispersion has a solid content of at least about 15%.

26. The golf ball of claim 24, wherein the solvent-borne dispersion has a solid content of at least about 30%.

27. The golf ball of claim 24, wherein the solvent-borne dispersion has a viscosity of about 300 cps to about 1,500 cps.

28. The golf ball of claim 24, wherein the solvent-borne dispersion has a viscosity of about 500 cps to about 1,000 cps.

29. The golf ball of claim 24, wherein the solvent-borne dispersion has a viscosity of about 700 cps to about 900 cps.

30. The golf ball of claim 1, wherein the barrier layer is applied using spraying or dipping.

31. A golf ball comprising a core, a barrier layer enveloping the core, and a cover enveloping the barrier layer, wherein:

the barrier layer has a moisture vapor transmission rate less than that of the cover; and

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the barrier layer comprises aluminum flakes comprising aluminum oxide.

32. A golf ball comprising a core, a barrier layer enveloping the core, and a cover enveloping the barrier layer, wherein:

the barrier layer has a moisture vapor transmission rate less than that of the cover; and

the barrier layer comprises a means for creating a hydrophobic tortuous path across the barrier layer.

33. A golf ball comprising:

a core having a diameter of at least about 1.62 inches;

a barrier layer of less than about 0.02 inches thick enveloping the core; and

a cover of less than 0.03 inches thick enveloping the barrier layer, wherein the barrier layer has a moisture vapor transmission rate less than that of the cover.

34. The golf ball of claim 33, wherein the barrier layer comprises a thermoplastic or thermoset composition of microparticles dispersed in a binder.

35. The golf ball of claim 34, wherein the microparticles comprise aluminum flakes comprising aluminum oxide, and the binder comprises at least one styrenic polymer.

36. The golf ball of claim 34, wherein the composition further comprises a cross-linking agent, a catalyst, or a coupling agent.

37. The golf ball of claim 34, wherein the composition is dispersed in a non-aqueous solvent system comprising aromatic hydrocarbons, ketones, acetates, alcohols, or esters.

38. The golf ball of claim 34, wherein the composition has a particle-to-binder weight ratio of about 0.5 to about 2.5.

39. The golf ball of claim 33, wherein the barrier layer has a moisture vapor transmission rate of less than about 0.95 grams·mm/(m²·day).

40. The golf ball of claim 33, wherein the thickness of the barrier layer is about 0.002 inches to about 0.007 inches.

41. The golf ball of claim 33, wherein the core has:

a diameter of about 1.62 inches to about 1.64 inches;

a compression of less than about 100;

a deflection at 100 kg of greater than about 1.5 mm;

a coefficient of restitution of greater than about 0.78; and

a specific gravity of less than about 1.4 g/cm³.

42. The golf ball of claim 33, wherein the core comprises:

a polybutadiene having a Mooney viscosity of greater than about 35;

a crosslinking agent in an amount of greater than about 15 parts per 100 parts by weight of the polybutadiene; and

an optional plasticizer.

43. The golf ball of claim 33, wherein the core comprises:

a center having a diameter of about 0.5 inches to about 1.6 inches, a compression of about 10 to about 100, a deflection at 100 kg of greater than about 1.5 mm; and

an outer core layer enveloping the center.

44. The golf ball of claim 43, wherein the center comprises:

a polybutadiene having a Mooney viscosity of greater than about 35;

a crosslinking agent in an amount of about 15 part to about 40 parts per 100 parts by weight of the polybutadiene;

a regrind or filler; and

an optional plasticizer.

45. The golf ball of claim 43, wherein the outer core layer comprises:

a polybutadiene having a Mooney viscosity of greater than about 35;

a crosslinking agent in an amount of about 25 part to about 55 parts per 100 parts by weight of the polybutadiene;

a regrind, polyisoprene, or filler; and

an optional plasticizer, wherein the outer core layer has a material hardness of greater than about 60 Shore C.

46. The golf ball of claim 33, wherein the cover has an outermost surface occupied by about 250 to about 450 dimples, and comprises:

a composition formed from a thermoplastic polyurethane, a thermoset polyurethane, a thermoplastic polyurea, or a thermoset polyurea; and

the composition having a material hardness of about 25 Shore D to about 65 Shore D and a flexural modulus of at least about 2,000 psi.

47. The golf ball of claim 33, wherein the golf ball has:

a compression of less than about 110;

a coefficient of restitution greater than about 0.79;

a moment of inertia greater than about 84 g·cm²; and

a deflection at 100 kg of greater than about 1.5 mm.

* * * * *

**DECLARATION OF THOMAS L. HALKOWSKI
IN SUPPORT OF CALLAWAY GOLF'S
MOTION *IN LIMINE* TO EXCLUDE
ACUSHNET'S "TEST BALLS" AND RELATED
TESTIMONY**

EXHIBIT 5

REDACTED
DOCUMENT

**DECLARATION OF THOMAS L. HALKOWSKI
IN SUPPORT OF CALLAWAY GOLF'S
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EXHIBIT 6

REDACTED
DOCUMENT